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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

CORROSION OF SILICATE GLASSES BY ALKALINE SOLUTIONS

COMMUNICATION 2. RELATION BETWEEN THE STABILITY OF GLASSES TO ALKALI AND THEIR COMPOSITIONS

V. S. Molchanov and N. E. Prikhid'ko

All silicate materials are broken down to some extent when treated with alkaline solutions. This is due mainly to the breakdown and consequent solubilization of complex oxygen-silicon radicals that are linked with metals in silicates and also to the solubilization of uncombined silica present in many silicate materials, e.g. glasses. The readiness with which various forms of silica are attacked by alkalis is related to the density of packing of atoms in their structures; the more orderly the arrangement of atoms and the greater the density of packing, the lower is the rate of destruction. This can be seen from the results of Molchanov and Ozeretskovskaia [1], Pike and Hubbard [2], and the authors of this paper [3], who compared rates of dissolution in alkalis for crystalline and vitreous quartz and for minerals consisting of various forms of hydrated silica. The highest stability is possessed by crystalline quartz, which may be regarded as the limiting member of this series.

With increased openness of structure (quartz glass) and with increased hydration (opals), the resistance of silicate materials to the action of alkalis falls. Since complex silicate glasses can be represented as combinations of silica and silicates, their variation in alkali-stability can be treated from the above point of view. The diminution in the density of packing of atoms and the simplification of the composition of the silicon-oxygen radicals (a peculiar form of depolymerization) probably explain the regular fall in alkali-stability with diminution in silica content observed by Molchanov and Ozeretskovskaia [1] for multicomponent glasses. The same was found by Dubrovo and Shmidt [4] for simple sodium silicate glasses. It was noted that the relation of the rate of attack by alkali to the silica content is always represented by substantially the same curve for many complex glasses containing various combinations of alkali metals, barium, lead, and zinc [1]. This shows that, in comparison with other components, silica plays the leading role in determining the alkali-stability of the glass. There are some other components, however, which have a considerable effect on this property. This is particularly true of zirconium and beryllium. The natural orthosilicates of these metals, zircon and phenacite, are sharply distinguished from other silicates in their alkali- and acid-stabilities [5]. Correspondingly, zirconium-containing glasses [3, 6] are extremely alkali-stable; more so, in fact, than quartz glass. As regards the similar effect of beryllium, only less reliable data are available in patent [7].

Some elements that may be present in silicates or silicate materials, though not having the exceptional effect of zirconium, nevertheless may make it possible to preserve the alkali-stability at a roughly constant level in spite of the reduced silica content resulting from the replacement of silica by the oxide of the metal introduced. Only when the concentration of the added element attains considerable proportions does the stability begin to fall. Such an effect was established for aluminum by Kitaigorodskii and Lande [8] and Dubrovo and Shmidt [4], for titanium by Sawai and Usidima [9] and later Bezborodov and Kisel' [10], for zinc by Cherniak [11], and for calcium by Bezborodov [12]. There are references to the higher alkali-stability of glasses containing lanthanum (Hamilton, Grauer Zabawsky, and Hahner [13]). It should be noted, however, that the last investigation was carried out with complex glasses containing also beryllium, whereas the other authors were concerned with simpler glasses for which the composition was varied in a regular manner. The effects of some other elements, apart from those referred to above, on the alkali-stability of glasses (magnesium, barium, lead, boron, iron, manganese) were characterized to some extent in the classical work of Turner and Dimbleby [14]. However, these authors studied mainly glasses in which the added element was introduced into the original glass (80 % SiO_2 + 20 % Na_2O) not in replacement of silicon,

but in replacement of sodium, which is of less interest for practical purposes.* Turner and Dimbleby noted the peculiar behavior of boron; for this element there is a sharply marked optimum concentration (about 10 %, expressed as boron trioxide) for which the alkali-stability of the glass is at a maximum. Glasses containing more or less than this amount are of considerably lower stability. In a less notable form the same sort of behavior is shown by barium, large additions of which lower the alkali-stability of the glass. It is probable that similar observations could be made for other elements, but this would require their addition to glass in amounts lying far outside the range of compositions of practical glasses. At the low concentrations studied by Turner and Dimbleby the added elements caused increased alkali-stability of the binary glass, but at medium concentrations the alkali-stability was not affected. It was of interest to determine whether silicon can be replaced by still other elements without appreciable lowering of the alkali-stability of the glass, and we undertook an investigation into this matter.

EXPERIMENTAL

We examined silicate glasses varying in composition in a systematic way and determined rates of destruction by alkaline solutions. Most of the experiments were carried out with glasses for which the composition could be expressed in the form $(87 - x)\%SiO_2 + x\%RO + 13\% Na_2O$ (compositions are expressed as mole percent throughout). The sodium content was kept constant, and silica was replaced by 5, 12, 17, 22, 27, and 32% of the oxide of the bivalent metal. The oxides used were those of beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, and lead.** Clear beryllium glasses could be obtained only with 12, 17, and 22% of beryllium oxide. We studied also some binary sodium silicate glasses containing 13-33% of Na_2O. Finally, on the basis of a light flint glass of composition 14% Na_2O, 9% PbO, 77% SiO_2 we studied the effect of the replacement of PbO by TiO_2. Most of the glasses were made in a flame furnace in 1-liter and 3-liter quartz crucibles, but the binary sodium glasses containing 85.7, 80.0, and 66.7 % Na_2O were prepared in a platinum crucible in a laboratory electric furnace. The raw materials fulfilled the purity requirements for the batch ingredients of optical glasses. When the melting was complete the glass mass was homogenized by stirring with an iron hook or by churning; the glass prepared in a platinum crucible was stirred with a platinum stirrer. The glasses were cast into bars, which were cooled in an annealer from 450° or 550°. Samples were cut from the bars and were ground and polished in the usual way.

TABLE 1

Thickness of Dissolved Layer (microns) of Glasses of the Type $(87 - x)SiO_2 \cdot xRO \cdot 13Na_2O$

Mole percent (x)	RO							
	BeO	MgO	CaO	SrO	BaO	ZnO	CdO	PbO
5	—	1.1	1.3	1.8	1.7	1.5	1.0	1.7
12	0.9	1.4	0.9	2.2	2.0	2.0	1.3	2.0
17	1.0	1.5	1.0	2.3	2.5	2.4	1.3	2.4
22	0.8	1.7	1.0	1.8	2.9	2.7	1.3	3.2
27	—	1.5	1.4	2.3	3.0	2.9	1.4	5.2
32	—	1.9	1.6	2.8	4.5	3.5	1.5	7.2

The destructive agent used was 0.5 N NaOH. The degree of destruction of the glass was characterized by the thickness of the layer dissolved in four hours from a surface of about 0.5 sq. cm by 950 ml of the alkaline solution at 90°, the sample under test being rotated at 200 r.p.m. The thickness of the layer of glass dissolved was determined with the aid of an MII-1 interference microscope from the displacement of the interference bands at the boundary between attacked and unattacked areas of glass. When the thickness of the dissolved layer was more than 8 μ, the MIS-11 double microscope was used. The thickness measurements were accurate within ± 5.0 %. Details of the procedure are given in our first communication [3]. The results are given in Tables 1-3. In the examination of Table 1 the data must be compared with the thickness of the dissolved layer of the "control" glass (13 % Na_2O), which is given in Table 2.

* The presence of alkali metals in glasse greatly facilitates its manufacture and working. In practice, therefore, there is a tendency to use the greatest possible amount of alkali components compatible with satisfactory durability of glassware produced.

** For all glasses 0.3 % of As_2O_3 was added to the batch to facilitate removal of bubbles from the melt.

TABLE 2

Thickness of Dissolved Layer (microns) of Binary Sodium Silicate Glasses

% SiO_2	87	85.7	84	80	75	66.7
Na_2O : SiO_2	1 : 6.7	1 : 6	1 : 5.25	1 : 4	1 : 8	1 : 2
Thickness of layer	1.1	1.3	1.7	3.2	10.9	69

TABLE 3

Thickness of Dissolved layer (microns) of Glasses of the Type $77SiO_2 \cdot (9 - x)PbO \cdot x\,TiO_2 \cdot 14Na_2O$

% TiO_2 in glass (x)	0	3	6	9
Thickness of layer	2.3	1.3	1.1	1.8

Although some individual figures are somewhat out of line with the rest, which is bound to occur owing to the small absolute values of the thickness of the dissolved layer, to departures of the actual compositions of glasses from those calculated from synthesis data, and to casual errors, the results enable us to establish the following:

1. In glasses containing a constant sodium oxide content of 13 %, much of the silica (up to 22 %) can be replaced by any of the bivalent-metal oxides investigated with practically no change in the alkali-stability of the glass. With further increase in the amount of silica replaced, there is a gradually increasing fall in stability and differences between the different metals begin to appear. Thus, the introduction of barium and lead reduce the alkali-stability to a greater extent, and the introduction of cadmium to a smaller extent, than the introduction of other metals.

2. The effect of alkaline-earth metals is in accord with the ionic-radius rule*: the stability of the glass falls with increase in the ionic radius of the metal introduced in place of silicon. In other words, bivalent metals can be placed in a series according to the extent to which they reduce the stability of the glass: Be < Mg < Ca < < Sr < Ba. For the pair zinc and cadmium the ionic-radius rule is not applicable, for cadmium glasses are considerably more stable than zinc glasses.

3. Binary sodium silicate glasses containing less than 20 % of Na_2O have alkali-stabilities that are quite comparable with those of more complex glasses. This gives us reason to suppose that the above conclusions apply also to glasses containing more soda (and also to glasses less rich in alkali) than was present in the glasses that we studied (13 %). Taking account of the fact that the fall in the alkali-stability of ternary glasses begins at an RO content of 22 %, we may consider that, in general, all complex silicate glasses apart from those containing boron will have about the same stability to the action of caustic alkalis if their silica contents are not below 65%. When components such as La, Ce, Li, and Ta are introduced, cases of enhanced stability will be met.

4. The results on the effect of the replacement of lead by titanium on the stability of sodium-lead glasses suggest that the behavior of titanium is similar to that of the other metals studied so that the conclusions in paragraphs 1-3 can be extended to titanium.

SUMMARY

1. The alkali-stabilities of glasses of the type (87 - x)%SiO_2, x%RO, 13%Na_2O (R is Be, Mg, Ca, Sr, Ba, Zn, Cd, or Pb), binary sodium silicate glasses containing 13-33 moles %Na_2O, and titanium-containing flint glasses were determined by measuring the thickness of the dissolved layer interferometrically.

2. It was shown that, with the exception of beryllium oxide, all oxides introduced into the binary glass in place of silica lower the alkali-stability of the glass. At first (up to 22 % RO), the lowering is only slight and

* This series appears to have been first noted by Miuller and Vainshtein [16] in the case of the rate of dissolution of alkaline borate glasses in water; it was then confirmed in the work of Academician Grebenshchikov's school on the breakdown of silicate glasses by hydrofluoric and hydrochloric acids and by atmospheric moisture [1].

the glasses differ little in alkali-stability. When the amount of silica replaced by metal oxide is higher than this, there is a considerable fall in stability; this fall is the greater, the greater the ionic radius of the metal introduced (ionic-radius rule).

3. For sodium oxide contents of up to 20 moles percent, binary sodium silicate glasses are fairly stable. Titanium affects stability to alkali in the same way as lead.

LITERATURE CITED

[1] V. S. Molchanov and O. S. Molchanov, Trans. State Optical Inst. No. 146, 1956.

[2] R. Pike and D. Hubbard, J. Res. Nat. Bur., Stand. 50, No. 2, 87 (1953).

[3] V. S. Molchanov and N. E. Prikhid'ko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1151. *

[4] S. K. Dubrovo and Iu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 403. *

[5] A. G. Betekhtin, Mineralogy, State Geol. Press, Moscow, 1950.**

[6] O. K. Botvinkin and B. V. Tarasov, Glass and Ceramics, No. 7, 7 (1954).

[7] German Patent 710079, abstracted in Glas. Techn. Ber. 19, 402 (1941).

[8] I. I. Kitaigorodskii and L. S. Lande, in the Collection "Effect of Composition on the Physicochemical Properties of Glasses," Trans. State Glass Inst., Moscow, 1954, p. 27.

[9] I. Sawai and H. Usidima, abstracted in Glas. Techn. Ber. 20, 235 (1942).

[10] M. A. Bezborodov and I. I. Kisel', Proc. Acad. Sci. USSR, 103, 1073 (1955).

[11] M. G. Chemiak, Effect of Composition on the Physicochemical Properties of Glass, Trans. State Glass Inst., Moscow, 1934, p. 64.

[12] M. A. Bezborodov, J. Soc. Glas. Techn. 28, 113 (1944).

[13] E. Hamilton, O. Grauer, Z. Zabawsky and C. Hahner, J. Am. Ceram. Soc. 31, No. 5, 132 (1948).

[14] W. Turner and V. Dimbleby, J. Soc. Glas. Techn., 10, 304 (1926); 12, 52 (1928).

[15] H. Wessel, Silikattechnik 3, No. 11, 483 (1952).

[16] R. L. Miuller and Ts. V. Vainshtein, J. Phys. Chem. 7, No. 3, 364 (1936).

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SOLID SOLUTIONS IN THE SYSTEM Al_2O_3–SiO_2

N. A. Toropov and F. Ia. Galakhov

The phase diagram of the system Al_2O_3–SiO_2, which is particularly important for the interpretation of various physicochemical processes occurring in the firing, fusion, and crystallization of various aluminum silicate refractories, has often been the subject of investigation. In the first variant of this phase diagram, published by Shepherd, Rankin, and Wright [1] in 1909, one chemical compound was described, this being an analog of the natural mineral sillimanite having composition $Al_2O_3 \cdot SiO_2$ with a congruent melting point of 1816°.

Wright noted heterogeneity in the structure of crystals of synthetic sillimanite, which generally contained glassy inclusions and had refractive indices that differed from those of natural sillimanite. These observations prompted an investigation by Bowen and Greig [2], published in 1924. The chemical compound formed by components of the system was assigned the new formula $3Al_2O_3 \cdot 2SiO_2$, and the melting of this was described as incongruent. This compound, being identical in composition with a natural mineral found on the island of Mull in Scotland, was called mullite. Thus, on the phase diagram there was now one eutectic instead of two and a new reaction point had appeared.

In 1951, in the course of a study of the ternary system BaO–Al_2O_3–SiO_2 we observed primary crystallization of mullite in the region directly adjacent to the figurative point for mullite, which was contrary to Bowen and Greig's phase diagram of the system Al_2O_3–SiO_2. In a special investigation we showed that mullite has a congruent melting point [3]. In the new variant of the phase diagram there was a maximum corresponding to the melting point of mullite, and there was a eutectic between mullite and corundum.

Further investigations of Budnikov, Tresviatskii, and Kushakovskii [4], carried out by the method of heating and cooling curves, confirmed the congruent character of the melting of mullite.

Barta and Barta [5] prepared monocrystals containing 67.69–99.69 % of Al_2O_3 by Verneil's method for alumina-silica mixtures. On the basis of their results and those of other authors they consider that solid solutions exist between the compositions of sillimanite and $2Al_2O_3 \cdot SiO_2$, which they named pragite. These authors are in agreement with our view on the congruent character of the melting of mullite.

By x-ray method it was shown by Posnjak and Greig [6] and by Rooksby and Partridge [7] that mullite can form solid solutions with alumina. According to Rooksby and Partridge, the maximum alumina content of such solid solutions is about 77.5 %, which corresponds to the formula $2Al_2O_3 \cdot SiO_2$. These authors call mullite of composition $3Al_2O_3 \cdot 2SiO_2$ "α-mullite" and mullite of composition $2Al_2O_3 \cdot SiO_2$ "β-mullite."

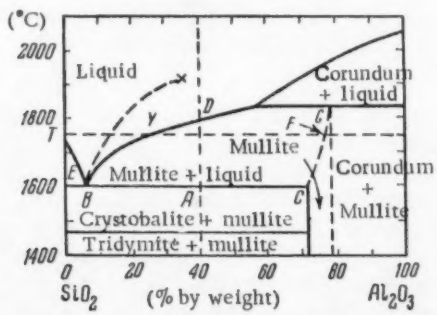

Fig. 1. Al_2O_3–SiO_2 phase diagram constructed by Sheers and Archibald.

Sheers and Archibald [8], on the basis of the x-ray results of Posnjak and Greig and of Rooksby and Partridge on the existence of solid solutions of mullite, made corrections in the phase diagram for Al_2O_3–SiO_2 given by Bowen and Greig. The corrected diagram (Fig. 1) gives a tentative indication of the position of mullite solid solutions in the system. There are serious doubts about the accuracy of this diagram: first, it is in conflict with the fact, which we have established, that mullite melts without decomposition, and, second, it has not been verified experimentally by studying the crystallization of the appropriate mixtures.

The experiments described below were carried out in order to verify the existence of solid solutions, the limits of their existence, and the correspondence of the results obtained with the variant of the phase diagram that we have developed previously.

EXPERIMENTAL

In 1950 one of us [9] designed a microfurnace having a tungsten element for temperatures up to 2000°. After being modernized, this furnace can now attain 2500°; heating can be carried out not only in a vacuum, but also in an inert gas, and the sample can be quenched. The temperature was measured with a voltmeter indicating the p.d. across the furnace, and this was graduated by means of samples of known melting point ($CaO \cdot Al_2O_3$ — 1600°; Pt — 1773°; Al_2O_3 — 2050°). Melting and other visible changes in the sample were observed through an observation tube having a removable lens.

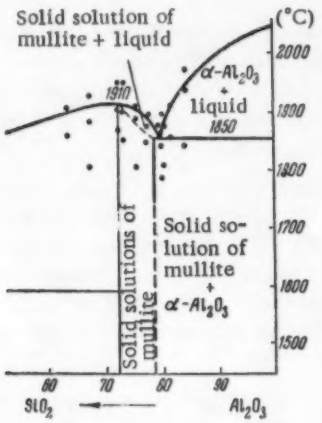

Fig. 2. Al_2O_3—SiO_2 phase diagram obtained in the present investigation.

The samples were prepared from alumina prepared from ammonium alum in which only traces of impurities could be detected spectroscopically and from powdered crystal quartz containing 99.90% of SiO_2. The mixtures were moistened with dextrin solution, pressed into the form of thin rods, and fused in an electric arc.

The investigation was carried out by the widely known method of quenching. A sample measuring 2-3 mm was placed on a tungsten wire and heated in the furnace until completely melted. The temperature was then raised by 100-200° for further homogenization with formation of a uniform liquid phase, after which the required temperature was established and maintained for a period of from 20 seconds to 10 minutes. With the aid of a magnet the sample was then thrown into the cold zone of the furnace. The exceptionally high rate of crystallization of our melts enabled us to confine ourselves to extremely short times for the separation of crystalline phases from the melt and the development of sufficiently large crystals. The quenched samples were observed under the microscope in the form of polished sections and immersion preparations.

Ten samples containing 62-83 % of alumina were prepared. The results of quenching experiments, which are given in the table, were used for the construction of the phase diagram (Fig. 2). Owing to the high rate of crystallization in samples quenched from temperatures above the liquidus, glass was either absent, or was present in very small amount. However, the crystals that separated during cooling were very small and were readily distinguished from the large crystals that separated during the period at a temperature below that of the liquidus. Hence, in the column headed "Phases" in the table, "glass" may be marked with an asterisk: this means that the liquid phase actually crystallized, fully or partially, during quenching.

The solidus line for mullite solid solutions could not be established exactly owing to the rapid crystallization of the residual liquid in equilibrium with the solid phase. It is here impossible to be guided by the sizes of the crystals as in the case of the determination of the liquidus. The solidus for the solid solution is therefore shown on the diagram as a broken line. The solidus line for corundum was established from the temperature of the eutectic between corundum and mullite solid solution. Photomicrographs of polished sections of quenched samples are shown in Fig. 3.

In general form the liquidus line is in close accord with that established in our previous work [3]. The eutectic between mullite solid solution and corundum has the composition 79 % Al_2O_3 and 21 % SiO_2. The limiting composition found for the solid solution of mullite and alumina, 78 % Al_2O_3, is in good agreement with the results of other investigators. We found no mixed crystals between mullite $3Al_2O_3 \cdot 2SiO_2$ and sillimanite $Al_2O_3 \cdot SiO_2$, the existence of which were postulated by Barta and Barta. In Samples 4 (composition of sillimanite) and 9 (lies between mullite and sillimanite) quenched from various temperatures a considerable amount of glass was always present. The amount of glass was approximately the amount calculated from the phase diagram now presented. If mixed crystals existed in this region, the glass should be absent for the range 1600-1830°. We consider, there-

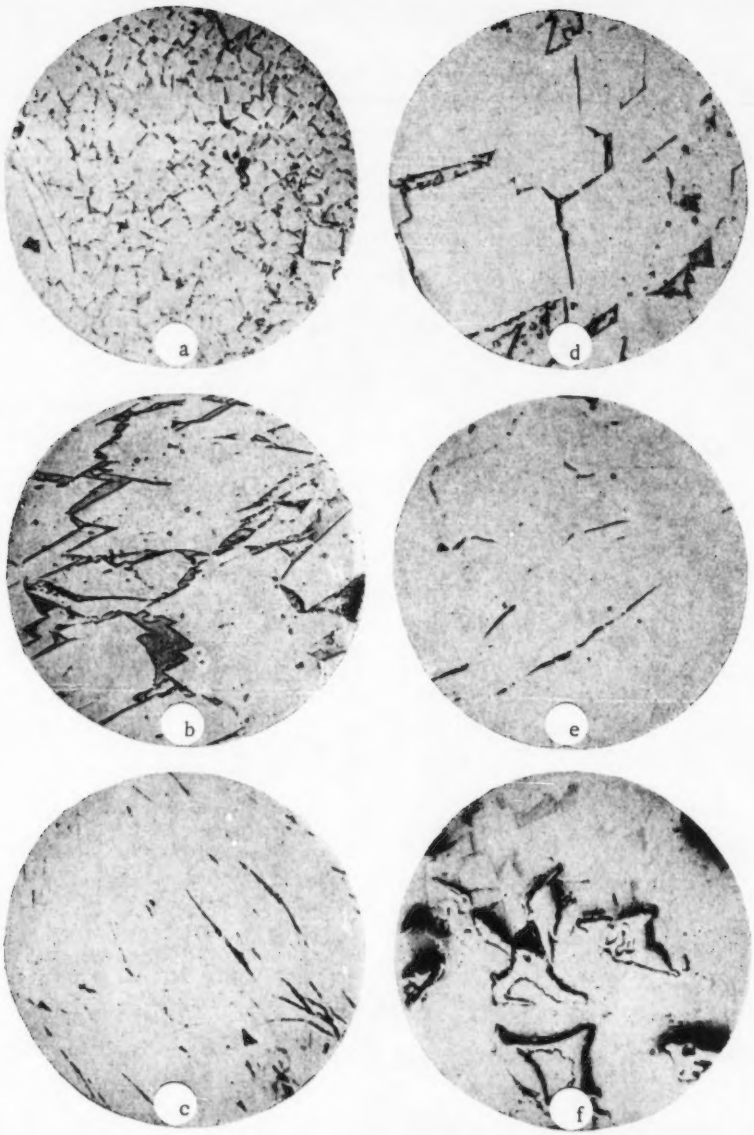

Fig. 3. Photomicrographs of quenched samples. Reflected light; X 410. Composition: Al_2O_3 — 71.8 %; SiO_2 — 28.2 %; a) fine mullite separated in quenching from 1940° (20 seconds); b) coarse mullite, glass (1900°, 20 seconds) (for complete crystallization a longer period is necessary). Composition: Al_2O_3 — 77.5 %; SiO_2 — 22.5 %; c) aggregates of fine mullite separated in quenching (1890°, 30 seconds); d) coarse mullite, glass (1870°, 30 seconds) . Composition: Al_2O_3 — 80%; SiO_2 — 20%; e) aggregates of fine mullite separated in quenching (1890°, 30 seconds); f) corundum, fine mullite, separated in quenching (1870°, 30 seconds).

fore, that the question of the existence of sillimanite-mullite solid solutions requires further experimental verification.

TABLE

Results of Quenching Experiments on the System Al_2O_3–SiO_2

Sample No.	Composition (% by weight) Al_2O_3	SiO_2	Temp. (°C)	Time	Phases
4	62.9	37.1	1900	30 sec.	Glass*
			1850	30 »	Mullite + glass
			1750	10 min.	Mullite + glass
9	67	33	1920	40 sec.	Glass*
			1880	40 »	Mullite + glass
			1800	2 min.	Mullite + glass
1	71.8	28.2	1940	20 sec.	Glass*
			1900	20 »	Mullite + glass
			1860	20 »	Mullite + glass
			1750	10 min.	Coarse and fine mullite + glass (very little)
8	72.3	27.7	1940	30 sec.	Glass*
			1900	30 »	Mullite + glass
			1840	30 »	Mullite +glass (very little)
7	75	25	1900	30 »	Glass*
			1880	30 »	Mullite + glass (very little)
			1800	30 »	Mullite + glass (very little)
2	77.5	22.5	1890	30 »	Glass*
			1870	30 »	Mullite + glass (very little)
			1840	30 »	Mullite + glass (very little)
10	79	21	1870	90 »	Glass*
			1830	30 »	Corundum + mullite + glass (very little)
			1780	40 »	Corundum + mullite + glass (very little)
3	80	20	1890	30 »	Glass*
			1870	30 »	Corundum + glass*
			1800	30 »	Corundum + mullite
6	81	19	1900	30 »	Glass*
			1850	30 »	Corundum + glass*
			1770	30 »	Corundum + mullite
5	83	17	1970	20 »	Glass* (very fine mullite + + glass
			1940	20 »	Corundum + glass*
			1830	20 »	Corundum + mullite

SUMMARY

1. The high-alumina part of the system Al_2O_3–SiO_2 was investigated by the method of annealing and quenching.

2. On the basis of the results a new phase diagram was constructed. This shows the position of mullite solid solutions.

3. The congruent character of the melting of mullite was again confirmed.

LITERATURE CITED

[1] E. S. Shepherd, G. A. Rankin and W. Wright, J. Am. Sci. 28, 302 (1909).

[2] N. L. Bowen, and I. W. Greig, J. Am. Cer. Soc. 7, 238 (1924).

[3] N. A. Toropov and F. Ia. Galakhov, Questions of Petrography and Mineralogy, Vol. 2, Izd. AN SSSR, p. 245, 1953.*

[4] P. P. Budnikov, S. G. Tresviatskii, and V. I. Kushakovskii, Proc Acad. Sci. USSR, 93, 2, 281 (1953).

* In Russian.

[5] R. Barta and Ch. Barta, J. Appl. Chem. No. 3 (1956).*

[6] E. Posnjak, I. W. Greig, J. Am. Cer. Soc. 16, 569 (1933).

[7] H. P. Rooksby, and I. H. Partridge, J. Soc. Glass. Techn. 23, 338 (1939).

[8] E. C. Sheers, W. A. Archibald, Iron Steel 27, 1-2, 26, 61 (1954).

[9] F. Ia. Glakhov, Works Lab. 2, 254 (1951).

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THERMOCHEMICAL DETERMINATION OF BOND ENERGIES

COMMUNICATION 1. Sn—C BOND ENERGIES IN TETRAMETHYL- AND TETRAETHYLTIN

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Knowledge of the energies of the bonds between atoms of reacting parts of molecules and the atoms of the catalyst surface is of great importance for the method, which is now being developed on the basis of the multiplet theory, of the scientific selection of catalysts, which is destined to replace obsolete empirical methods of discovering catalysts [1]. The available data on bond energies which can be used in the multiplet theory for the calculation of the adsorption potentials of catalysts is very incomplete and requires substantial supplementation. In particular, there is an almost complete absence of information on the energies of bonds formed by C, H, O, and N with elements entering the composition of the most important catalysts. Hence, apart from the determination of bond energies by the kinetic method [2], it has become urgently necessary to begin a systematic study of bond energies of importance in catalysis by the thermochemical method, i.e. by the experimental determination of heats of combustion of compounds containing bonds whose energies can be used in calculating energy barriers of reactions and adsorption potentials.

Values of metal-carbon bond energies, which are particularly valuable in the study of the catalysis of organic compounds over metal catalysts, can be obtained from the heats of combustion of the corresponding organometallic compounds. However, calorimetric measurements in this field present great difficulties [3, 4], and great demands are made on the experimental technique. In order to investigate the applicability of our method of determining the heats of combustion of organometallic compounds, we made measurements on two comparatively stable compounds, tetramethyl- and tetraethyltin. The results of the investigation, apart from their importance for the study of the method, are of interest in themselves in that, in the case of tetraethyltin, the value found for the heat of combustion, and therefore the value found for the Sn—C bond energy, differs from reported values and is more nearly in accord with the regular variation in bond energy in the homologous series of tetraalkylmetals [4].

EXPERIMENTAL

As the purity of the original compounds is of great importance in calorimetric determinations of bond energies, special attention was paid to the synthesis of the compounds and their purification.

The tetraalkyltins were synthesized through the organomagnesium compounds as indicated:

$$SnCl_4 + 4AlkMgI \longrightarrow Sn(Alk)_4$$

In view of variations in the literature regarding details of the synthesis and of the purification of the teraalkyltin, we describe our procedures, which we adopted on the basis of a critical examination of data in the literature [5-12].

Tetramethyltin was prepared [11] by reaction between 0.44 mole of freshly distilled $SnCl_4$ (b.p. 114°) and CH_3MgI (2.68 moles of Mg and 2.61 moles of CH_3I) in 6 moles of ether. The CH_3MgI solution was decanted from residual magnesium [6]. After the addition of the $SnCl_4$ the reaction mixture was boiled for four hours; ether was then distilled off and the residue was heated for four hours at 140-160°. The ether solution obtained was concentrated and shaken with an aqueous-alcoholic solution of KF. The filtrate was washed with water, dried over calcium chloride, and fractionated through a column (30 theoretical plates). The fraction of b.p. 76-78° (760 mm) was collected. The solution of the product in dry ether (1 : 5) was treated with dry ammonia, the precipitate was

filtered off [10], and the product was fractionated through a column, dried over phosphoric oxide, and again fractionated. Reaction for halogen was negative [7].

Tetraethyltin was synthesized [5-7, 11], like tetramethyltin, by reaction between 0.22 mole of $SnCl_4$ and C_2H_5MgBr (1.50 moles of C_2H_5Br and 1.52 moles of Mg). After the addition of the $SnCl_4$ the mixture was boiled for one hour, most of the ether was distilled off, and the residue was heated at 100°. To the cooled mixture one-half of the ether that had been distilled off was added, and decomposition was effected by successive treatments with water, ammonium chloride solution, and dilute hydrochloric acid. The purification of the product was analogous to that of tetramethyltin. It was dried over phosphoric oxide and fractionated through a column (b.p. 178--178.5°). It was then cooled to -120° and the precipitate was filtered off [7]. The product was dried over sodium and fractionated over sodium through a column: b.p. 178-178.5° (748 mm). This fraction was vacuum-fractionated through a column: b.p. 80° (7 mm).

TABLE 1

Physical Constants of Tetramethyl- and Tetraethyltin

Substance	B.p. in °C (p in mm)	d_4^t	n_D^t	
$Sn(CH_3)_4$	76 (720)	1.3138 (0°)	1.4393 (21°)	According to data in literature [6, 11, 12, 13]
	76—77 (720)	1.29136 (25.5°)	1.52009 (25.5°)	
	77 (720)			
	78 (760)			
	78.3 (740)			
$Sn(C_2H_5)_4$	76 (733)	1.2995 (20°)	1.4421 (20°)	According to our data
	39.5 (2)	1.1913 (25°)	1.4719 (20°)	According to data in literature [5, 6, 7, 10, 11, 14, 15]
	78 (13)	1.1916 (25°)	1.4702 (23°)	
	93.5 (26.5)	1.1988 (19.7°)	1.4696 (25°)	
	175 (760)		1.4717 (20°)	
	175—177 (760)		1.4693 (25°)	
	176—177 (749)		1.4724 (19.7°)	
	176—177 (760)			
	80 (7)	1.1953 (20°)	1.4722 (20°)	According to our data
	178—178.5 (748)			

The physical constants of tetramethyl- and tetraethyltin and their Raman spectra are given in Tables 1 and 2.

The spectra were determined on a three-prism Steinchel spectrograph. The illuminant consisted of three IGAR-2 lamps, total wattage 1500. In both cases the exposure was four hours on Eastman II-O plates.

The method of measuring heats of combustion and the design of the calorimetric apparatus used are described in papers of Skuratov and coworkers [17]. The calorific value of the calorimetric system was determined by the combustion of standard benzoic acid (VIIM, Leningrad). The isothermal (20°) heat of combustion of this benzoic acid was taken as 6324 $cal_{15°}$ per gram. The temperature of the calorimeter was read accurately within 0.0003° with the aid of a supersensitive mercury thermometer and a special optical tube. The substance was burnt in thin-walled ampoules weighing 0.2-0.3 g placed in thin-walled quartz basins with lids (weight not more than 1 g). A new quartz basin was used in each experiment because the SnO_2 formed stuck firmly to the walls of the basin. The main difficulty in the combustion of the substances was spattering and incomplete combustion, and this made it necessary to carry out numerous preliminary experiments to determine the most favorable combustion conditions (selection of the type of glass for the construction of ampoules, the weight of the ampoule and the extent to which it should be filled, etc.) All necessary corrections were made in the calculation of the results: for heat exchange, for heat of formation of HNO_3, for heat of combustion of the igniting material, for the nonisothermal character of the combustion process, and for the thermal correction of the exposed mercury column. The weight of materials was reduced to the weight in a vacuum. As the SnO_2 formed in the combustion was in the crystalline state and the other products were those obtained in the combustion of organic substances of composition $C_aH_bO_c$, it was easy to make Washburn's correction, which adjusts the heat of combustion at an initial pressure of 30 atm to a pressure of 1 atm, both for the reactants and for the products. The heat of formation of an aqueous solution of HNO_3 from N_2, O_2, and liquid H_2O was taken to be 13.81 kcal/mole, and the heat of combustion of the iron ignition wire was

taken to be 1792 cal/g [18]. Table 3 gives the heats of combustion of the substances investigated.

TABLE 2

Raman Spectra of Tetramethyl- and Tetraethyltin

No.	Data in literature for $Sn(CH_3)_4$ (cm^{-1})			Our data (cm^{-1})	
	Pai [16]	Siebert [12]	Lippincott [13]	$Sn(CH_3)_4$	$Sn(C_2H_5)_4$
1	152 (7)	151 (10)	150 (10)	146.2 (7)	249.25 (3)
2	262 (4)				480.2 (10)
3	506 (8)	506 (10)	507 (10)	508.78 (10)	506.4 (10)
4	526 (5)	525 (8)	532 (10)	527.9 (10)	594.75 (0)
5		769 (1)	772 (2)	724.56 (0)	717.6 (0)
				780.3 (0)	
6	952 (0)				959.25 (4)
7	1046 (0)		1053 (1)		1014.8 (6)
					1056.5 (0)
8		1197 (10)	1194 (10)	1193.5 (10)	1190.9 (10)
9	1200 (5)		1205 (10)	1200.1 (10)	1241.1 (0)
					1282.95 (0)
10	1262 (0)			1329.8 (1)	1329.8 (1)
					1382.0 (1)
11		1434 (2)	1451 (2)	1402.7 (1)	1423.12 (3)
					1451.2 (4)
12	2915 (3)	2909 (8)	2912 (6)		1466.65 (4)
				2839.0 (1)	2822.0 (0)
13	2979 (2)	2982 (6)	2988 (5)	2872.5 (6)	2870.5 (6)
				2916.0 (7)	2916.0 (7)
				2941.5 (4)	2930.0 (5)
				2980.0 (0)	

*Frequencies of 700 cm^{-1} and less can be attributed to tetrahedral, fully symmetrical and deformation vibrations. Here the most intense frequencies are 508.78 and 527.9 cm^{-1} for $Sn(CH_3)_4$ and 480.2 and 506.4 cm^{-1} for $Sn(C_2H_5)_4$. The double line 959.25-1014.8 cm^{-1}, which is observed only for $Sn(C_2H_5)_4$, may be attributed to the characteristic vibration of the ethyl group. Lines from 1056.5 to 1382.0 cm^{-1} can be ascribed to bending vibrations of CH_3 groups in trimethyltin and CH_2 and CH_3 groups in tetraethyltin. The frequencies from 1402.7 to 1466.65 cm^{-1} are deformation vibrations $\delta(CH_2)$ and $\delta(CH_3)$; those from 2822.0 to 2980.0 cm^{-1} must be attributed to valence vibrations $\nu(CH_2)$ and $\nu(CH_3)$ [for the CH_2 groups of $Sn(C_2H_5)_4$ and the CH_3 groups of $Sn(C_2H_5)_4$ and $Sn(CH_3)_4$].

TABLE 3

Heats of Combustion of $Sn(CH_3)_4$ and $Sn(C_2H_5)_4$

Substance	$-\Delta H_l^{20}$ (kcal/mole)	Heat of evaporation (kcal/mole)	$-\Delta H_g^{20}$ (kcal/mole)
Tetramethyltin	905.7	8.2	913.9
Tetraethyltin	1545.9	11.8	1557.7

The figures in the second column of Table 3 are enthalpy changes in the isothermal (20°) combination of the investigated substances in the liquid state with gaseous molecular oxygen at a pressure of 1 atm, the products being $SnO_2(s)$, $H_2O(l)$, $CO_2(g)$, and $N_2(g)$, also at 1 atm. The relative error in the measurements (mean departure of the results from the arithmetical mean) in our determinations was 0.05 %.

In the third column of Table 3 we give heats of evaporation, which were estimated with the aid of Klages's empirical equation [19]:

$$\lambda_{25} = 5.4 + 0.036\,t,$$

in which t is the boiling point(°C). In the fourth column we give heats of combustion of the substances investigated, calculated for the gaseous state.

In order to make sure that in the final state, after the combustion of tetramethyl- and tetraethyltin, tin is present as the dioxide without any admixture of the monoxide or free metal, x-ray structure analysis was carried out on the combustion products* and it was established that combustion proceeds as far as tin dioxide. The values of the x-ray lines are given in Table 4.

TABLE 4

Results of x-Ray Structure Analysis (A)

No.	Combustion product	Data in literature [20]		
		SnO_2	SnO	Sn
1	3.36 (8)	3.34 (10)		
2	2.62 (8)	2.64 (6)	2.66 (2.5)	
3	2.34 (5)	2.36 (2)	2.39 (0.5)	
4	2.30 (1)			
5	1.742 (10)	1.75 (6)	1.79 (3)	
6	1.668 (6)	1.67 (1)		1.65 (2)
7	1.619 (1)		1.59 (4)	
8	1.580 (3)	1.58 (0.5)		
9	1.492 (6)	1.49 (1)	1.48 (1.5)	1.48 (2)
10	1.435 (6)	1.435 (1)		1.45 (2)
11	1.407 (6)	1.412 (1.5)		
12	1.319 (5)	1.315 (0.6)		1.33 (0.5)
13	1.211 (10)	1.213 (1)	1.22 (0.5)	
14	1.176 (8)	1.18 (0.2)		1.20 (2)

The value that we obtained for the heat of combustion of tetramethyltin in the liquid state was $-\Delta H_1^{20} = 905.7$ kcal/mole, which is close to the value obtained by Lippincott [13]: $-\Delta H^{25} = 903.5 \pm 10$ kcal/mole. On the other hand the value found for the heat of combustion of tetraethyltin was 1545.9 kcal/mole, which is considerably higher than that given by Norrish [3] (1523 kcal/mole).

For the strict calculation of heats of formation at the standard temperature of 25° the experimental data for 20° must be recalculated for 25°. As calculation showed,** the correction required lies within the limits of accuracy of our measurements. From the heats of formation obtained standard heats of formation of tetramethyl- and tetraethyltin from elements and from atoms were calculated. The following values of heats of formation were assumed: $\Delta H^{25}_{CO_2(g)} = 94.052$ kcal/mole; $\Delta H^{25}_{H_2O(l)} = 68.317$ kcal/mole; $\Delta H^{25}_{SnO_2(s)} = 138.8$ kcal/mole; and heats of atomization of tin, hydrogen, and graphite: $\Delta H^{25}_{Sn} = 70$ kcal/g-atom; $\Delta H^{25}_{H_2} = 104.2$ kcal/mole; $\Delta H^{25}_{C} = 138$ kcal/g-atom. The first three values are taken from the tables of the US Bureau of Standards [22], the heat of atomization of tin is taken from [23], and the heats of atomization of hydrogen and graphite are taken from Cottrell's monograph [4]. It should be noted that some authors accept the value of 171 kcal/g-atom for the heat of atomization of carbon. This question has not been finally resolved. We took heats of sublimation from Cottrell in order to be able to use the modern system of bond energies given by this author.

TABLE 5

Heats of Formation of $Sn(CH_3)_4$ and $Sn(C_2H_5)_4$

Substance	$-\Delta H^{25}$ from elements (kcal/mole) (liquid)	$-\Delta H^{25}$ from elements (kcal/mole) (gas)	$-\Delta H^{25}$ from atoms (kcal/mole) (gas)
Tetramethyltin	19.2	11.0	1260.1
Tetraethyltin	28.5	16.7	2234.5

* The authors thank A. M. Rubinshtein, in whose laboratory the x-ray structure analysis was carried out.

** Specific heats of liquid tetramethyl- and tetraethyltin were obtained by extrapolation of Staveley's data [21]: $c_p = 72.6$ kcal/mole·deg for tetramethyltin and $c_p = 55.0$ kcal/mole·deg for tetraethyltin.

Table 5 gives heats of formation of the investigated substances from elements and from atoms. In Table 6 the results are compared with the values given in the literature [3] for the heats of formation of tetraalkyltins in the liquid state.

TABLE 6

Comparison of Our Values of Heats of Formation with Those Given in the Literature

Formula of substance	$-\Delta H^{25}$ (kcal/ mole)		Difference in heats of formation of successive homologs	
	data in literature [3]	our data	data in literature [3]	our data
$Sn(CH_3)_4$	17	19.2		
$Sn(C_2H_5)_4$	49	28.5	32	9
$Sn(C_3H_7)_4$	56		7	28
$Sn(C_4H_9)_4$	94		38	
$Sn(C_5H_{11})_4$	132		38	

It will be seen from Table 6 that, if instead of the value for the heat of formation of tetraethyltin found previously [3] we write the value obtained in the present investigation, the difference in heats of formation of successive homologs becomes regular, which suggests that our results are more reliable.

The average Sn—C bond energies in teramethyl- and tetraethyltin were calculated by the additive scheme from heats of formation from atoms, it being assumed that the atoms present in the molecule are in their ground states and not in excited states. The C—C and C—H bond energies were taken as 66.2 and 90.5 kcal/ mole, respectively. Calculation in this way gives the Sn—C bond energy in tetramethyltin as 43.0 kcal/ mole and that in tetraethyltin as 39.0 kcal/ mole.

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SUMMARY

1. The heats of combustion of tetramethyl- and tetraethyltin were determined and their heats of formation from their elements and the Sn—C bond energy were calculated. The heats of formation found introduced greater regularity in the homologous series than the results of previous investigators.

2. It was shown that the calorimetric procedure used is suitable for the determination of heats of combustion of organometallic compounds with a sufficiently high degree of accuracy. However, an individual approach is necessary to the combustion procedure to be applied in the case of every compound investigated, and it is therefore necessary to carry out numerous preliminary experiments.

3. The Raman spectrum of tetraethyltin was determined for the first time.

LITERATURE CITED

[1] A. A. Balandin, J. Gen. Chem. 16, 793 (1946).

[2] A. A. Balandin and A. A. Tolstopiatova, J. Phys, Chem. 30, 1367, 163 (1956).

[3] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. A 187, 337 (1946).

[4] T. Cottrell, Strengths of Chemical Bonds (Russian translation), Foreign Lit. Press, 1956).

[5] P. Pfeiffer and K. Schnurrmann, Ber. 37, 319 (1904).

[6] E. Krause, and A. V. Grosse, Die Chemie der Metallverbindungen, 1937.

[7] L. A. K. Staveley, and H. P. Paget, J. Chem. Soc, 1950, 2290.

[8] E. Krause, Ber. 51, 1447 (1918).

[9] L. A. K. Staveley, J. Chem. Soc. 1917, 1992.

[10] G. Grüttner and E. Krause, Ber. 50, 1808 (1917).

[11] Z. M. Manulkin, J. Gen. Chem. 5, 281 (1935); 11, 386 (1941).

[12] H. Siebert, Z. anorg. Chem. 263, 82 (1950); 268, 177 (1952).

[13] E. R. Lippincott, and M. C. Tobin, J. Am. Chem. Soc. 75, 4141 (1953).

[14] K. A. Kocheshkov, J. Gen. Chem. 4, 1359 (1934).

[15] H. Körschig, Z. Naturforsch. 1, 219 (1946).

[16] N. G. Pai, Proc. Roy. Soc. 149, 29 (1935).

[17] S. M. Skuratov, A. A. Strepikheev and O. N. Kachinskaia, Sci. Mem. Moscow State Univ. 164, 73 (1953).

[18] J. E. Hawkins, and W. T. Eriksen, J. Am. Chem. Soc. 76, 2669 (1954).

[19] F. Klages, Ber 82, 358 (1949).

[20] A. I. Kitaigorodskii, x-Ray Structure Analysis of Finely Crystalline and Amorphous Substances, Moscow and Leningrad, GTTI, 1952.

[21] L. A. K. Staveley, J. B. Warren, H. P. Paget and D. J. Dowrick, J. Chem. Soc. 1954, 1992.

[22] Select. Values of Chem. Thermod. Prop., Washington, 1952.

[23] L. Brewer, R. F. Porter, J. Chem. Phys. 21, 2012 (1953).

[24] K. J. Laidler, Canad. J. Chem. 34, No. 5, 626 (1956).

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USE OF RADIOCARBON FOR COMPARING THE RATES OF DEHYDROGENATION OF BUTANE AND BUTENE

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In our investigation [1] of the dehydrogenation of butane-butene mixtures, in which we used radiocarbon C^{14}, reaction was carried out in presence of a special catalyst under conditions favorable for the formation of butadiene. It was shown that the butadiene was formed from butene, whereas conversion of butane into butadiene hardly occurred at all. It was concluded that the formation of butadiene from butane must pass through the stage of the formation of butene and its desorption from the surface, so that the desorption of butene cannot be the limiting stage of the overall reaction. This conclusion can be amplified by investigating dehydrogenation over another catalyst under conditions favorable for the dehydrogenation of butane.

In the present investigation we made further calculations, based on data from the previous investigation [1], of relative rates, the rate of formation of butadiene from butane being compared quantitatively not only with the rate of formation of butadiene from butene, but also with the rate of formation of butene from butane. We also carried out special experiments over an alumina-chromia catalyst [2] under conditions favorable to dehydrogenation of butane, and these made it possible to elucidate the above-considered questions regarding the dehydrogenation of butane-butene mixtures for this catalyst.

Calculation of Rates of Dehydrogenation over a Chromium Oxide Catalyst

Let us examine the following reaction scheme:

$$\begin{array}{ccc} \overset{\alpha}{C_4H_{10}} & \xrightarrow{w_1} & \overset{\beta}{C_4H_8} \\ & {\scriptstyle w_2}\searrow \quad \swarrow{\scriptstyle w_3} & \\ & \underset{\gamma}{C_4H_6} & \end{array} \qquad (1)$$

We have shown previously that the rate w_2 is extremely small in comparison with w_3. In order to determine more accurately the extent to which w_2 is less than w_3, we shall make use of the values of the specific activities of butane, butene, and butadiene from Table 1 [1] and of the amount of butadiene (millimoles per liter of original gas) from Table 2 [1]. Fig. 1 is constructed from the data in these tables. Curve 1 gives the relation of butadiene concentration to time of contact, and Curve 2 shows the variation of the specific activity of butene. The following equation:

$$\gamma = \frac{1}{\tau}\left[x\int_0^{\tau}\alpha d\tau + (1-x)\int_0^{\tau}\beta d\tau\right] \qquad (2)$$

enables us to calculate specific activities of butadiene as a function of time of contact τ for various values of w_2/w_3. In Equation (2) α, β, and γ are specific activities of butane, butene, and butadiene, and x is the fraction of the butadiene that is formed from butane. On the assumption that x varies very little under the conditions of our experiments

$$\frac{x}{1-x} = \frac{w_2}{w_3}. \qquad (3)$$

The curves in Fig. 2 give calculated values of γ for $\underline{x} = 0.01$, 0.002, 0.001, and 0.0001, which correspond to $w_2/w_3 = 1/100$, $1/500$, etc.; the points are values of γ from Experiments 21-23 (Table 1 [1]). As will be seen these points lie near the curve corresponding to $\underline{x} = 0.001$. Hence, the rate of formation of butadiene from butene is of the order of a thousand times as high as the rate of formation of butadiene from butane. Values of w_1 (Scheme (1)) for times of contact ranging from 1 to 3 seconds were calculated in [1] (Table 3) and averaged at 0.04mmole/ /second liter.

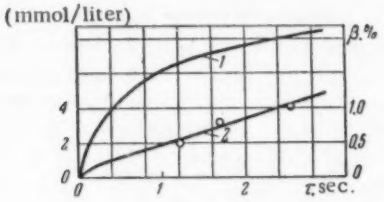

Fig. 1. Relation of 1) butadiene concentration (mmoles/ liter of original gas) and 2) specific activity of butene to time of contact in Experiments 24-26 (chromium oxide catalyst, [1]).

Fig. 2. Relation of specific activity of butadiene to time of contact calculated from Equation (2) for various values of $\underline{x}$. The points are experimental data from Experiments 24-26 [1].

The value of w_3 in Scheme (1) can be determined from the experimental data given in Table 2 of the paper [3]. In accordance with theory, Scheme (1) yields an expression determining the value of w_3 in the form [1, 3]:

$$w_3 = \frac{d\gamma}{d\tau} \frac{c_1}{(\gamma - \beta)} . \qquad (4)$$

The values of β, γ, and $d\gamma/d\tau$ can be determined graphically from Fig. 3, which is constructed from the data in Table 2 [3]. Butadiene concentrations c_1 (millimoles per liter of original mixture) were given in Table 2

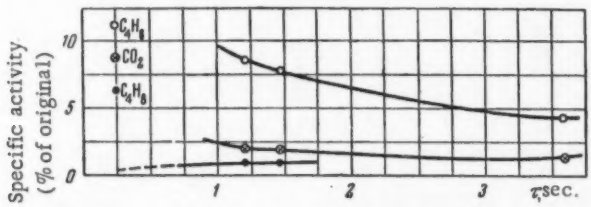

Fig. 3. Relation of specific activities of butadiene, carbon dioxide, and butene to time of contact in experiments with a chromium oxide catalyst.

[1]. The results of the calculation of the rate of dehydrogenation of butadiene w_3 are given in Table 1, from which it follows that w_3 is 2 mmoles/ second · liter. We thus obtain the relative values of all three rates in Scheme (1):

$$w_1 : w_2 : w_3 = 20 : 1 : 1000.$$

TABLE 1

Rate of Dehydrogenation of Butene (mmoles/ second · liter of original gas)

(Experiments 24-26)

τ sec.	c_1 (mmol/ /liter)	γ	β	$\gamma - \beta$	$-\frac{d\gamma}{d\tau}$	w_3
1.0	6.2	9.2	0.75	8.5	3.0	2.2
1.5	7.1	7.7	1.0	6.7	1.7	1.8

The relationship obtained confirms our previous conclusion [1], namely that butadiene is formed almost exclusively from butene. The rate of the direct conversion of butane into butadiene is actually small not only in comparison with the rate of conversion of butene into butadiene, but also in comparison with the rate of conversion of butane into butene, being not more than 5 % of the latter.

Dehydrogenation over an Alumina-Chromia Catalyst

In the investigation of the dehydrogenation of butane-butene mixtures over an alumina-chromia catalyst, the experimental procedure [1] was modified somewhat. The dried 1 : 1 mixture of butane and butene passed from the gas holder through the flow meter to the reactor, which contained 2 ml of catalyst. At the exit of the reactor there was a contact manometer which was connected through a relay to a Patrikeev rubber pump [4], which permitted working at a reduced pressure. The contact manometer was set for a definite pressure, which was maintained during the experiment by the automatic switching on and off of the pump. During the experiment the pressure was checked with a mercury manometer connected to the reactor. In other respects the procedure in the experiment and the analysis of the products was the same as in the previous work [1].

TABLE 2

Amounts of Reaction Products (mmoles/ liter of original gas)

Composition of original gas: butane 50 ±1%, butene 50 ± 1%. Temperature 600 ± 3°. Pressure 250 ± 5 mm.

Experiment No.	31	41	38	40	29	33
τ (sec.)	0.56	0.60	1.05	1.27	1.88	1.94
Substance	Amounts of reaction products (mmoles/ liter)					
C_4H_{10}	21.4	21.0	18.6	18.9	17.2	—
C_4H_8	18.0	16.9	15.7	15.7	15.1	—
C_4H_6	—	3.5	4.1	3.9	6.1	3.9
Carbonaceous deposits on catalyst	—	1.1	1.33	1.3	2.1	2.2
Total	—	42.5	39.7	39.9	40.5	—
As % on original		95.5	89.0	89.5	90.5	—

TABLE 3

Specific Activities of Reaction Products (% of original activity)

Composition of original mixture: butane 50 ± 1%, butene 50 ± 1%. Temperature 600 ± 3°. Pressure 250 ± 5 mm. Specific Activity of butane 412 ± 5 impulses/ minute · mg, or 100%.

Experiment No.	35	42	36	43	34	37
τ (seconds)	0.57	0.75	1.26	1.49	1.72	2.69
Product	Specific activity (%)					
C_4H_{10}	—	97	97	97	93.5	92.5
C_4H_8	7	—	10	12.4	17.5	12
C_4H_6	6.8	7.2	9.3	13.6	16.5	11.6
Carbonaceous deposits on catalyst*	11.5	14	19	—	13.0	—

* Carbonaceous deposits are expressed as millimoles of C_4 hydrocarbons.

Dehydrogenation was carried out at a pressure of 250 ± 5 mm and a temperature of 600 ± 3°. The gas formed in the reaction was fractionated in a Podbielniak apparatus. The fraction containing butane, butene, and butadiene was analyzed: the butadiene content was determined in a Bushmarin apparatus, and the butene and butane contents in a modified Orsat apparatus. In order to separate the reaction products and determine radioactivities, the C_4 fraction was brominated: butane was then separated in the pure state and butene and butadiene in the form of bromides.

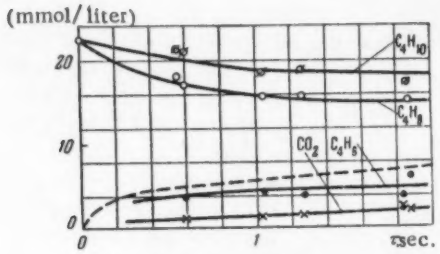

Fig. 4. Relation of concentrations of butane, butene, butadiene, and carbonaceous deposit (mmoles per liter of original gas) to time of contact for an alumina-chromia catalyst. The broken line represents the sum of the concentrations of butadiene and carbonaceous deposit.

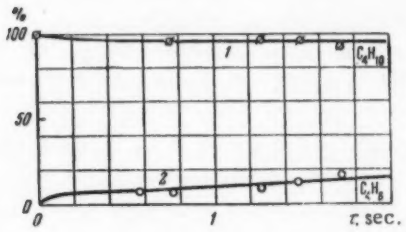

Fig. 5. Relation of specific activities of 1) butane and 2) butene to the time of contact in experiments with an alumina-chromia catalyst

As in previous investigations [1, 3], in addition to experiments with gas labeled with radiocarbon we carried out experiments with ordinary butane and butene. From these experiments we determined the dependence of the concentrations of butane, butene, and butadiene on the space velocity (time of contact). The results of these experiments are given in Table 2.

The carbonaceous deposits formed on the catalyst were removed after the experiment by passage of dry air freed from carbon dioxide. The carbon dioxide formed was absorbed in a U-tube containing ascarite, and in this way the amount of carbon associated with the catalyst was determined. In the experiments with radioactive gas, the carbon dioxide was absorbed in baryta water and the activity of the barium carbonate formed was determined. Table 2 gives the amount of C_4 hydrocarbons (millimoles per liter of mixture) remaining on the catalyst in the form of a carbonaceous deposit.

The specific radioactivities of butane, butene, butadiene, and carbon dioxide were determined in experiments with butane-butene mixtures in which the butane was labeled with radiocarbon. The specific activity of the original labeled butane was 412 ± 5 impulses per minute per mg of barium carbonate. The results of experiments with the mixture containing radioactive butane are given in Table 3.

The specific activities of butadiene and butene are always very close in value. To determine the extent of the conversion of butane into butadiene we shall use Scheme (1), Equation (2), and Figures 4 and 5. In Fig. 4 the total amount of butadiene and carbonaceous deposit formed is indicated by the broken line.

As we have previously [3] concluded that carbonaceous deposits are formed mainly from butadiene, the amount of butadiene actually formed should correspond to this broken line. The specific activity β of butene is found from Fig. 5. Fig. 6 gives the relation of specific activity of butadiene to time of contact calculated from Equation (2) for values of x = 0.1, 0.05, 0.04, and 0.01. As will be seen from Fig. 6, already at x = 4% the specific activity γ of butadiene must be appreciably higher than the specific activity of butene. Coincidence of values of β and γ occurs only at $x < 0.04$. Hence, over an alumina-chromia catalyst under conditions favorable for the dehydrogenation of butane, more than 96 % of the butadiene is formed from butene, i.e. in Scheme (1) the rate ratio $w_3 / w_2 = 25/1$.

When we compare the rates w_1 and w_2, making use of the data of Tables 2 and 3 and Figures 4 and 5, we find that they are of the same order. From the broken line in Fig. 3 the rate w_3 in the range 0.5-1.5 second can be estimated as 1.6 mmoles/liter-second. The rate w_1 determined from the equation $w_1 = \frac{d\beta}{d\tau} \frac{c_2}{(\alpha - \beta)}$ (in which α and β are the specific activities of butane and butene, c_2 is the concentration of butene, and $d\beta/d\tau$ is determined from Fig. 1) is 1.1 mmoles/liter · second in the same range of τ (Table 4). The rates w_1, w_3, and w_2 are then related as 18 : 25 : 1. Thus the value of w_1/w_2 is of the same order as in the experiments described in the first part of this paper.

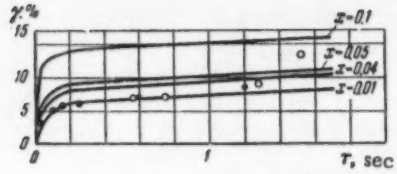

Fig. 6. Specific activity of butadiene calculated from Equation (2) for various values of x: ● – specific activities of butene (Curve 2, Fig. 4); o – specific activities of butadiene obtained experimentally.

TABLE 4

Values of Rates of Dehydrogenation of Butane to Butene, calculated from the Results of Experiments 34-43

τ(sec.)	c_3	α–β	dβ/dτ	w_1
0.5	17.4	90	6.0	1.2
1.0	15.8	87	6.0	1.1
1.5	15.2	84	6.0	1.1
2.0	15.0	80	6.0	1.1

Applying the results of the work of one of the authors and Kiperman [5] to the present case, we find that, if the rate constant for the dehydrogenation of butene at the surface is considerably less than the rate constants for the desorption of butene, hydrogen, and butadiene, then the constants in the denominator of the kinetic equation for catalytic dehydrogenation are adsorption coefficients.

The results of the present work confirm our previous conclusion [1], namely that the rate constant for dehydrogenation is much less than the rate constant for the desorption of butene. As the rate constants for the desorption of butene, hydrogen, and butadiene must be approximately of the same order, the rate constant for dehydrogenation must be considerably less than any of the constants for the desorption of the substances named above. Our experiments with labeled atoms therefore show that in the kinetic equation for dehydrogenation the constants in the denominator have the classical meaning of adsorption coefficients.

SUMMARY

1. With the aid of butane labeled with radiocarbon, the dehydrogenation of butane-butene mixtures was investigated over an alumina-chromia catalyst. The relative rates of the dehydrogenation of butane and butene to butadiene in presence of a chromium oxide catalyst were calculated from experimental data obtained previously.

2. It was shown that the ratio of the rates of dehydrogenation of butane to butene and of butane to butadiene is of the same order for the two catalysts and has a value of about 20 : 1. In experiments with the chromium oxide catalyst the ratio of the rates of formation of butadiene from butane and from butene is 1 : 1000, whereas in experiments with the alumina-chromia catalyst this ratio is 1 : 25.

3. It was confirmed that the formation of butadiene from butane proceeds through the stage of butene, which, before being converted further into butadiene, is desorbed from the surface into the bulk phase to an extent of not less than 95 %.

4. It was shown that the constants in the denominator of the kinetic equation for dehydrogenation are adsorption coefficients.

LITERATURE CITED

[1] A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isaguliants, A. P. Shcheglova and E. I. Popov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 157.*

[2] R. C. Archibald and B. S. Greensfelder, Ind. Eng. Chem. 37, 356 (1945).

[3] A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isaguliants, A. P. Shcheglova and E. I. Popov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 270.*

[4] V. V. Patrikeev, Works Lab. No. 10, 1269 (1947).

[5] A. A. Balandin and S. L. Kiperman, J. Phys. Chem. 31, 139 (1957).

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OXIDATION-REDUCTION SYSTEMS FOR THE INITIATION OF FREE-RADICAL PROCESSES

COMMUNICATION 8. MECHANISM OF THE ACTION OF A SYSTEM CONTAINING ETHYLENEDIAMINE AND A HYDROPEROXIDE

G. P. Belonovskaia, B. A. Dolgoplosk, Zh. D. Vasiutina, and M. N. Kulakova

Among numerous oxidation-reduction systems now used for the initiation of emulsion polymerization, systems consisting of polyethylenepolyamines, hydroperoxides, and iron salts [1-4] occupy an important place. In recent years papers on the mechanism by which such systems act have appeared [5-7]. In these, as in some earlier papers, it is stated that the systems are effective only when iron salts are present and that the function of the iron salt is to form a complex with the polyamine that will react readily with the hydroperoxide with formation of free radicals.

The authors envisage the following tentative schemes for the mechanism of the action of polyamine systems:

1. $[R'NH_2Fe^{2+}] + ROOH \rightarrow RO\cdot + HO^- + [R'NH_2Fe^{3+}]$
   $[R'NH_2Fe^{3+}] + HO^- \rightarrow HO\cdot + [R'NH_2Fe^{2+}]$ [6.7]
2. $[R'NH_2Fe^{2+}] + ROOH \rightarrow RO\cdot + R'NH\cdot + H_2O + Fe^{2+}$ [7.8]

Scheme 1 assumes catalytic action by a complex of the amine with a ferrous salt. Scheme 2 assumes that initiation of polymerization is associated with direct reaction between the amine and the peroxide with participation of ferrous iron. Neither scheme has found confirmation in the present investigation.

Kinetics of Reaction between the Hydroperoxide and Ethylenediamine in Aqueous Media in Presence of Iron Salts. The reaction between ethylenediamine and cumene hydroperoxide was carried out in aqueous solution at hydroperoxide and ethylenediamine concentrations of 0.5-1 % by weight. The kinetics of the reaction were characterized by the consumption of hydroperoxide, which was determined iodometrically. It was shown that the pH of the medium has a considerable effect on the rate of reaction between ethylenediamine and the hydroperoxide (Fig. 1); the optimum pH, at which the rate of the process is at a maximum, lies in the range 9.9-11.1. In further work, systems at a pH of 10.3-10.8 were always used. The presence of iron salts in the system is a determining factor for reaction between the hydroperoxide and ethylenediamine. It follows from Fig. 2 that the addition of only 0.05 mole % (on the hydroperoxide) of the iron pyrophosphate complex produces appreciable initiation of reaction at 0°. As already pointed out, in most previous investigations it has been supposed that a reactive iron complex of the amine plays a special part in the process. We have shown that the order in which the components of the system are mixed has a very great effect on the kinetics of the process. It follows from Fig. 3 (Curve 1) that, when the complex between ethylenediamine and the iron salt is prepared beforehand and the aqueous solution of the hydroperoxide is introduced into the system subsequently, reaction between the components is very slow at 0° and the solution has a stable yellow color. If, however, the iron salt is added to an aqueous solution of a mixture of equimolecular amounts of hydroperoxide and ethylenediamine or the amine is added to a mixture of the hydroperoxide and the iron salt, reaction is rapid and the solution has a deep-green color, which becomes yellow as the hydroperoxide becomes exhausted (Curve 2).

It is very interesting that addition of a fresh portion of iron salt to a system of low activity (Curve 1) activates the process, which then proceeds rapidly (Curve 3).

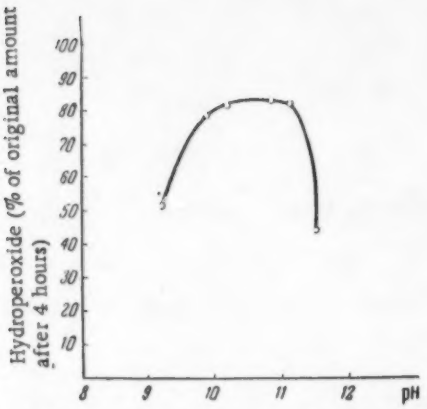


Fig. 1. Effect of the pH of the medium on the kinetics of the reaction of cumene hydroperoxide with ethylenediamine at 0° [1 mole Fe^{3+} to 100 moles of hydroperoxide; amine (moles) : hydroperoxide (moles) = = 1 : 1].

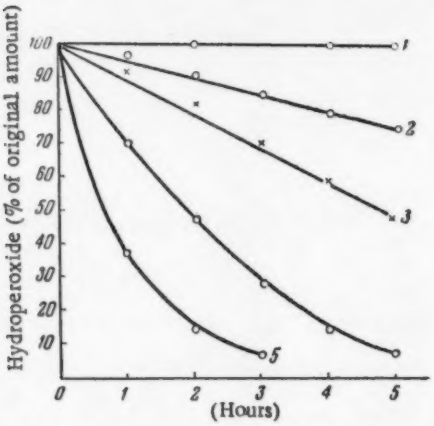


Fig. 2. Effect of concentration of Fe^{3+} pyrophosphate complex on the kinetics of reaction between the hydroperoxide and ethylenediamine [amine (moles) : hydroperoxide (moles) = 1 : 1; pH 10.7-10.8; 0°]; 1) iron absent; 2) 0.05 mole % Fe^{3+}; 3) 0.25 mole % Fe^{3+}; 4) 1.0 mole % Fe^{3+}; 5) 5.0 mole % Fe^{3+}.

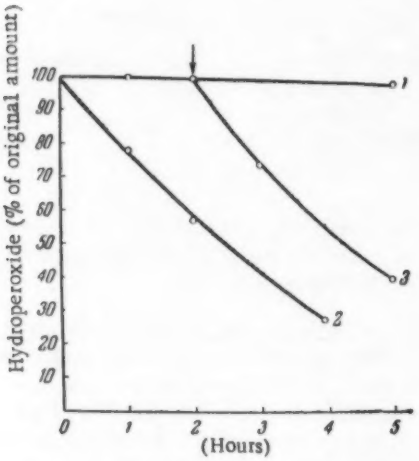


Fig. 3. Effect of order of mixing components on kinetics of the reaction of the hydroperoxide (hp) with ethylenediamine (ed) [ed (moles) : hp (moles) = 1 : 1; 0°; 1 mole Fe^{3+} to 100 moles of hp]: 1) (ed + Fe^{3+}) + hp; 2) (ed + hp) + Fe^{3+}; (hp + Fe^{3+}) + ed; 3) further Fe^{3+} added.

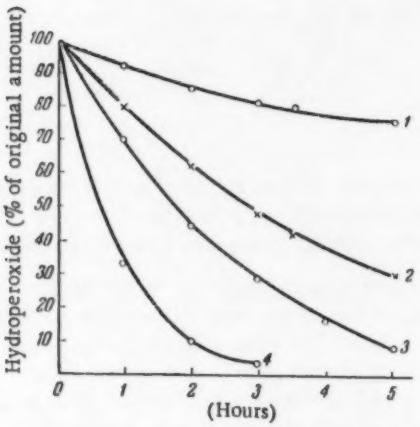


Fig. 4. Effect of molar ratio of ethylenediamine to the hydroperoxide on the kinetics of reaction between them (pH 10.3-11; 0°; 1 mole Fe^{3+} to 100 moles of hydroperoxide): 1) 1 : 8; 2) 1 : 2; 3) 1 : 4; 4) 1 : 0.25.

The results that we have cited provide convincing evidence of the necessity of the simultaneous presence of amine and hydroperoxide in the system at the moment of the formation of an active iron complex.

The relative amounts of amine and hydroperoxide greatly affect the kinetics of the process, which becomes more rapid as the mole fraction of amine increases (Fig. 4). At a molar ratio of ethylenediamine to hydroperoxide of 1 : 4 (1 molecule of hydroperoxide for each amine hydrogen atom), reaction in presence of methyl methacrylate at 20° proceeds almost to completion (Fig. 5, Curve 1). Curve 3 of this figure shows that the introduction of more hydroperoxide and iron pyrophosphate complex gives a system in which the concentration of hydroperoxide remains

unchanged for a long time, thus indicating absence of amines able to react with the hydroperoxide.

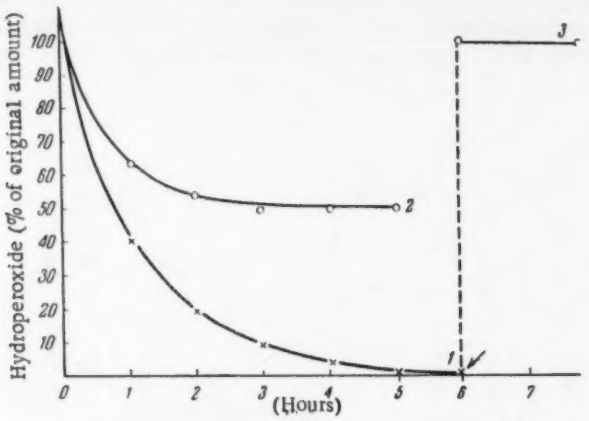
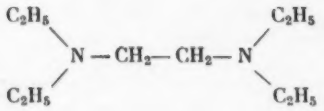


Fig. 5. Effect of molar ratio of ethylenediamine to cumene hydroperoxide (in presence of methyl methacrylate) (20°; pH 10.5): 1) 1:4; 2) 1:8; 3) more hydroperoxide added (⟶)

On the basis of these facts we may conclude that ethylenediamine and the hydroperoxide are consumed in stoichiometric amounts as a result of the direct participation of the amine hydrogens in the reaction. The participation of the amine hydrogens is confirmed by the fact that we could detect no reaction at all between tetraethylethylenediamine



and cumene hydroperoxide in presence of iron salts. It is confirmed also by the fact that at a 1 : 4 molar ratio of ethylenediamine to the hydroperoxide the pH falls from 10.5-11.0 at the start of the process to 7.5-7.0 at the finish. It was shown that in the course of the reaction the concentration of primary amino groups, as determined by van Slyke's method, diminishes. Thus, at a molar ratio of ethylenediamine to hydroperoxide of 1 : 4 in absence of methyl methacrylate, the concentration of primary amino groups fell by 57 % with a residual hydroperoxide content of 27 %. These results are in conflict with the views of Orr and Williams [6, 7], who on the basis of their results concluded that reaction with the hydroperoxide is of zero order with respect to the polyamine, which does not change in the reaction, but serves only for the protection of ferrous iron from oxidation. It was shown that the presence of monomer (methyl methacrylate) in the system has scarcely any effect on the kinetics of reaction at 0° (Fig. 6), which indicates that the chain stage of the process plays an insignificant part. This fact made it possible for us, in our further work, to study the kinetics of reaction between components of the system at 0° in absence of monomer. It was shown also that the presence of atmospheric oxygen in the system has no substantial effect on the kinetics of the process.

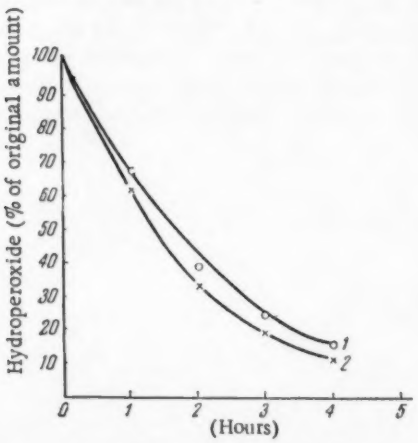


Fig. 6. Effect of monomer (methyl methacrylate) on the kinetics of reaction between the hydroperoxide and ethylenediamine [0°; 0.5 mole of Fe^{3+} to 100 moles of hydroperoxide; amine (moles) : hydroperoxide (moles) = 1 : 1]: 1) monomer absent; 2) monomer present.

Kinetics of Reaction between Components in Emulsion Media and the Kinetics of Polymerization.

In order to elucidate the mechanism of the action of the system under study it was necessary to establish the relation between the kinetics of the reaction of components in aqueous emulsions and the kinetics of polymerization. In preliminary work we showed that a system containing ethylenediamine, tert-butylcumene hydroperoxide, and an iron salt is fairly effective for the initiation of polymerization at + 5° when potassium "paraffinate" is used as emulsifier and the pH is maintained in the range 11.5-12.1. In 8-10 hours under these conditions the yield of butadiene-styrene copolymer was 60 %.

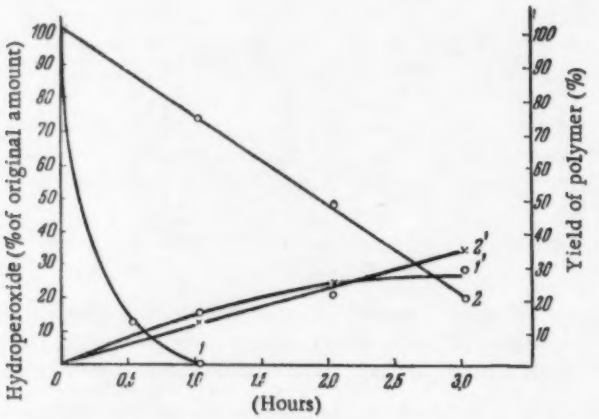


Fig. 7. Kinetics of the polymerization of styrene and of reaction between the components of the system (effect of order of mixing components) (+ 5°; 1 mole Fe^{3+} to 100 moles of hydroperoxide): 1,1') (hp + Fe^{3+}) + ed; 2,2') (ed + Fe^{3+}) + hp

We studied the reaction in an aqueous emulsion in which the hydrocarbon phase was a 1 : 1 mixture of ethylbenzene and styrene. We have pointed out the great effect of the order of mixing the components of the system on the kinetics of reaction in aqueous solutions. In the study of this factor under the conditions of emulsion polymerization it was shown that the same relation is found between the order of introducing the components of the system and the kinetics of the consumption of the hydroperoxide in the polymerization process (Fig. 7, Curves 1 and 2). On the basis of concepts regarding the formation of free radicals by reaction of the hydroperoxide with the amine it would be expected that the kinetics of the polymerization would have a definite connection with the kinetics of reaction between the components. However, it follows from Curves 1' and 2' (Fig. 7), and also from Fig. 8, that the kinetics of the polymerization of styrene and of the copolymerization of styrene with butadiene at 5° are almost independent of the kinetics of the decomposition of the hydroperoxide. It is extremely interesting also that the polymerization of styrene continues after the exhaustion of the hydroperoxide (Curves 1 and 1', Fig. 7).

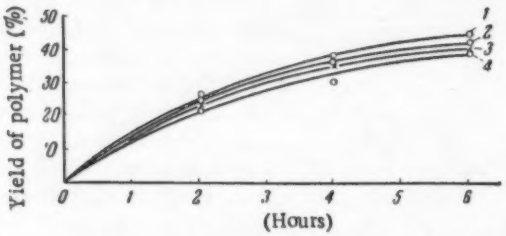


Fig. 8. Dependence of the kinetics of the copolymerization of 70 : 30 butadiene-styrene on the order of mixing of the components (5°; 0.5 mole of Fe^{3+} to 100 moles of hydroperoxide): 1) (ed + Fe^{3+}) + hp; 2) (hp + Fe^{3+}) + ed; 3) (hp + ed) + Fe^{3+}; 4) simultaneous introduction of components.

As in aqueous solutions, in polymerization in emulsions change in the iron concentration affects the rate of reaction between the components of the system. The decomposition of the hydroperoxide and the initiation of polymerization is observed in presence of traces of iron salts when the process is carried out in presence of potassium "paraffinate" prepared from vacuum-distilled "paraffinic acids." Addition to the system of very small amounts of iron salts (0.3-0.7 mole % on the hydroperoxide) greatly increases the rate of decomposition of the hydroperoxide (Fig. 9, Curves 1-3) while not having any substantial effect on the kinetics of polymerization (Curves 1'-3'). In this case also, polymerization continues after the complete exhaustion of the hydroperoxide in the solution.

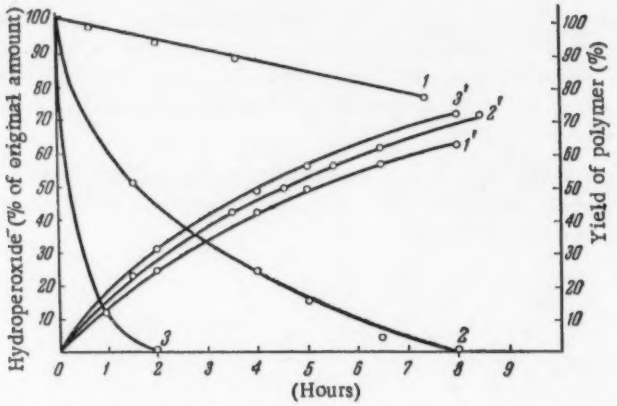


Fig. 9. Kinetics of the polymerization of styrene and of reaction between the components of the system (effect of iron concentration) (5°): 1,1') no supplementary addition of iron; 2,2') 0.3 mole % of Fe^{3+} (on hydroperoxide); 3,3') 0.7 mole % of Fe^{3+}.

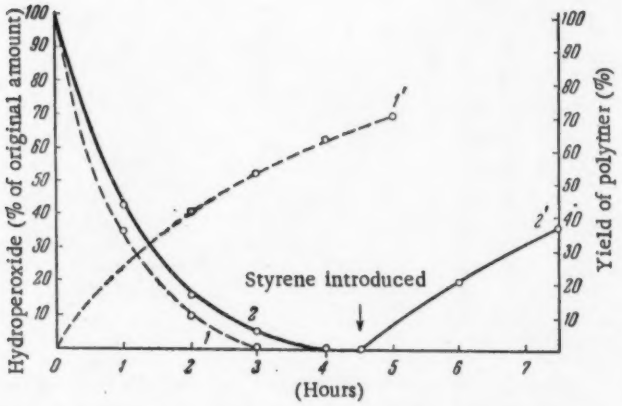


Fig. 10. Relation between decomposition of components of system and the polymerization of styrene (5°; 1 mole Fe^{3+} to 100 moles of the hydroperoxide): 1,1')reaction and polymerization in a system + + monomer; 2) reaction in a model system; 2') polymerization after reaction is complete.

It is evident, therefore, that there is no direct relation between the kinetics of reaction among components of the system and the kinetics of polymerization characteristic for many oxidation-reduction systems used for the initiation of free-radical processes.

These facts lead us to the conclusion that, as a result of reaction between ethylenediamine and the hydroperoxide in presence of iron salts, some new intermediate compounds are formed which are not of the peroxide

type but are able in some way to initiate polymerization. This conclusion was confirmed by special experiments on the possibility of initiating polymerization after the completion of the reaction between ethylenediamine and the hydroperoxide (after complete exhaustion of the latter). All the components of the initiating system (with ethylbenzene as hydrocarbon phase) were introduced into ampoules and, when the hydroperoxide had been completely consumed, the necessary amount of styrene was added. After definite intervals of time the amounts of polystyrene present in the ampoules were determined. Fig. 10 shows that when the hydroperoxide has been used up polymerization proceeds almost at the same rate as it did in presence of all components of the initiating system (Curves 1 and 1', Fig. 10).

Mechanism of the Action of the System. We concluded above that responsibility for the initiation of polymerization must be attributed to comparatively stable intermediate products that preserve their activity at 5° for a fairly long time. An idea of the nature of these intermediate products may be obtained from the composition of the products formed as a result of the decomposition of the hydroperoxide in presence of free-radical acceptors (monomer) or in their absence.

When cumene hydroperoxide reacts with ethylenediamine in aqueous solutions, gas evolution is observed to an extent which increases with rise in reaction temperature. Analysis of the gas shows that it is methane, the formation of which can be represented as follows:

$$C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot \rightarrow C_6H_5COCH_3 + CH_3\cdot \rightarrow CH_4$$

When small amounts of methyl methacrylate are added to the solution in order to trap the intermediate products (free radicals), the liberation of methane is suppressed completely (Fig. 11), which is in accord with the proposed scheme.

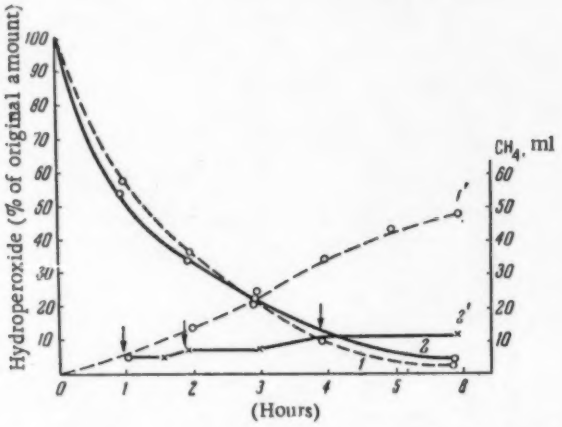


Fig. 11. Effect of an acceptor of free radicals (methyl methacrylate) on the liberation of methane in the reaction between the hydroperoxide and ethylenediamine [20°; ed : hp = 1 : 1 (moles); 0.025 mole Fe^{3+} to 100 moles of hydroperoxide]: 1, 1') decomposition of hydroperoxide and yield of CH_4 in absence of monomer; 2', 2) liberation of CH_4 in presence of methyl methacrylate and decomposition of hydroperoxide; the arrows indicate the introduction of methyl methacrylate.

Fig. 12 gives data on the kinetics of the decomposition of the hydroperoxide and on the liberation of methane at temperatures ranging from 5° to 70° (Fig. 12). It should be noted that at high temperatures (50-70°) the liberation of methane stops as soon as the hydroperoxide is exhausted, whereas at low temperatures it continues even when the hydroperoxide is used up, the behavior being in accord with the preservation of the activity of the system for the initiation of polymerization.

Investigation of the products formed after the complete consumption of the hydroperoxide at 0, 20, 50, and 70° showed that they consist mainly of acetophenone and α,α-dimethylbenzyl alcohol; their yield does not depend greatly on the temperature of the process and amounts to 55-65%.

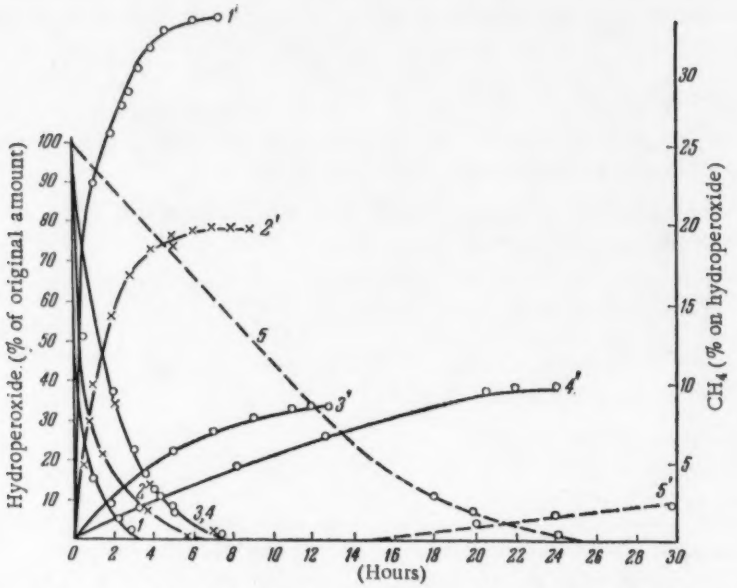


Fig. 12. Effect of temperature on the kinetics of reaction between the components and on the kinetics of the liberation of methane [ed : hp = 1 : 1 (moles); Fe^{3+} 0.025 mole % on hydroperoxide, except at 0° (0.05 mole %)]: 1, 1') 70°; 2, 2') 50°; 3, 3') 25°; 4, 4') 20°; 5,5') 0°.

The above scheme for the formation of methane implies equimolecular yields of methane and acetophenone. At low temperatures the yield of acetophenone is in fact considerably higher than that of methane. Only at 70° does the yield of methane approximate to that of acetophenone.

TABLE 1

Composition of Decomposition Products of the Hydroperoxide in its Reaction with Ethylenediamine in an Aqueous Medium in Absence of Monomer

[ethylenediamine : hydroperoxide = 1 : 1 (moles); 0.025 mole % of Fe^{3+} on the hydroperoxide]

Temperature of experiment (°C)	0	20	50	70
Methane (moles % on hydroperoxide)	6.5	10.5	19.1	32.7
Acetophenone (moles % on hydroperoxide)	40	39	39	46
α,α-Dimethylbenzyl alcohol (moles % on hydroperoxide)	15	15	17	19

It was necessary to determine whether the formation of acetophenone and α,α-dimethylbenzyl alcohol is associated with the intermediate reaction products, the free radicals. With this object, the decomposition products of the hydroperoxide, in presence and in absence of methyl methacrylate, were studied at 0° under conditions close to the polymerization conditions, i.e. at a molar ratio of ethylenediamine to hydroperoxide of 5 : 1 in presence of 0.5 mole % of Fe^{3+} on the amount of hydroperoxide.

The maintenance of the amount of acetophenone in presence of the monomer indicates directly that its formation is not associated with the free-radical stage of the process. The yield of α,α-dimethylbenzyl alcohol, unlike that of acetophenone, is substantially reduced in presence of methyl methacrylate. We must point out that increase in the mole fraction of ethylenediamine in the mixture results in a considerable increase in the amount of α,α-dimethylbenzyl alcohol in the product (25-28 % instead of 15%), whereas the concentration of acetophenone remains unchanged (about 40 %). It should be noted also that in this case the amount of methane liberated is considerably increased.

TABLE 2

Composition of Decomposition Products of Cumene Hydroperoxide in its Reaction with Excess of Ethylenediamine in Aqueous Solutions at 0°

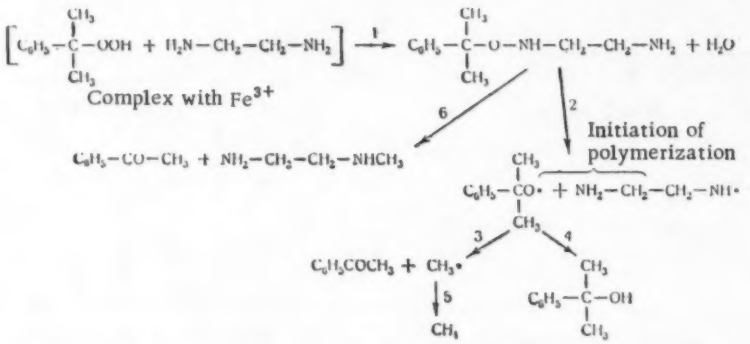
[ethylenediamine : hydroperoxide = 5 : 1 (moles); 0.5 mole % of Fe^{3+} (pyrophosphate complex) on the hydroperoxide]

Experimental conditions	Yield of acetophenone (moles % on hydroperoxide)	Yield of α,α-dimethylbenzyl alcohol (moles % on hydroperoxide)
In absence of methyl methacrylate	35-40	25-28
In presence of methyl methacrylate	34-40	14-15

It was shown above that reaction between the components of the system is accompanied by consumption not only of the hydroperoxide, but also of ethylenediamine in definite stoichiometric proportions. It was important in principle to establish whether any ethylenediamine fragments enter the polymer chain, which would give an unequivocal indication of the participation of radicals of the type RN· in the initiation of polymerization. With this in view methyl methacrylate polymers were prepared in a homogeneous aqueous medium at 0° and at 20°, and their nitrogen contents were determined. Before this determination the samples of polymethyl methacrylate were twice precipitated by methanol from dilute acetone solution and dried to constant weight. The molecular weights of the samples were determined cryoscopically (Table 3).

The results indicate that radicals of the type RN· participate in initiation of polymerization. We must mention here that in the preparation of polymers of low molecular weight the method of precipitation by alcohol which we used did not ensure complete separation of polymer, particularly the fractions enriched in ethylenediamine fragments. It is possible that this explains why nitrogen contents of polymer samples were lower than expected.

On the basis of all the experimental data cited we can suggest the following scheme in explanation of the character of the intermediate stages and the mechanism of the initiation of polymerization:



The formation of an unstable intermediate compound (by Reaction (1)) was established by Gambarian, Chaltykian, and others [9-12] for the reaction of benzoyl peroxide with aliphatic amines and can be explained by the mechanism proposed by Horner and Schlenk [13] for secondary aromatic amines and benzoyl peroxide.

The initiation of polymerization is probably associated with breakdown at the unstable O—N bond into radicals of the types $RO^{\cdot}$ and $RN^{\cdot}$ (Reaction (2)). In absence of monomer there occur Reaction (4), the formation of α,α-dimethylbenzyl alcohol (reaction of the $RO^{\cdot}$ radical with the amine), and Reactions (3) and (5), breakdown of $RO^{\cdot}$ with formation of acetophenone and the $CH_3^{\cdot}$ radical. The free-radical character of Reactions (4) and (5) is proved by the substantial reduction in the yield of α,α-dimethylbenzyl alcohol and complete suppression of the formation of methane in presence of an acceptor of free radicals, i.e. methyl methacrylate. The incomplete disappearance of α,α-dimethylbenzyl alcohol may be associated with an insufficiently high concentration of methyl methacrylate in the solution arising from its low solubility in water. It may be supposed that the main route by which acetophenone is formed is Reaction (6), without passage through the stage of free radicals.

The results of our work show that the usual treatment of the mechanism of the initiating action of oxidation-reduction systems in polymerization processes is in some cases not in accord with the main course of the process. As is well known, the action of oxidation-reduction systems in aqueous media is generally treated as follows:

1) $ROOH + HA \rightarrow RO^{\cdot} + H_2O + A^{\cdot}$ (in which HA is a reducing agent)

2) $ROOH + M^{2+} \rightarrow RO^{\cdot} + HO^{-} + M^{3+}$

It is supposed that the initiation of the chain process of polymerization is effected by free radicals that arise in the primary act of reaction between the peroxide and the reducing agent; in this process an energetically favorable factor is the formation of water or ions.

TABLE 3

Sample No.	Molecular weight (mean of 2 determinations)	Nitrogen content (%) (mean of 2 determinations)	Average number of nitrogen atoms in one polymer molecule
1	2500	0.3	0.5
2	2080	0.25	0.4
3	1500	0.35	0.5
4	970	0.46	0.3
5	1600	0.42	0.5
6	580	0.76	0.3
7	580	0.75	0.3

The present investigation showed that the primary oxidation-reduction process gives not radicals, but compounds that are less stable than the peroxide and undergo thermal decomposition into radicals. In this connection we may mention that Andakushkin, Dolgoplosk, and Radchenko [14], who studied the mechanism of the action of a system consisting of triazenes and various reducing agents, arrived at similar conclusions. Such systems formed the basis upon which oxidation-reduction initiation of polymerization was developed. However, after detailed study of this question these authors concluded that the initiation of polymerization is not associated with the oxidation-reduction act, but is the result of the formation of a new unstable compound, the alkanediazohydroxide, which decomposes thermally into free radicals. The possibility that an analogous mechanism operates also in other oxidation-reduction systems cannot be excluded.

EXPERIMENTAL

Reaction of Components of System in Aqueous Solutions

When aqueous solutions of cumene hydroperoxide [15] and ethylenediamine had been introduced into the apparatus in a nitrogen medium, a definite amount of the iron pyrophosphate complex was added. The process was considered to start from this moment. The hydroperoxide was determined by the iodometric method used previously for dilute aqueous solutions [16].

When reaction was carried out in presence of methyl methacrylate, before the start of the process 1 % by weight of methyl methacrylate was introduced into the reaction vessel and then, as polymer was precipitated, further portions of methyl methacrylate were added at definite intervals of time.

Reaction in an Aqueous Emulsion and the Kinetics of Polymerization

Reaction was carried out in an atmosphere of nitrogen in 40-ml ampoules with self-tightening stoppers of butyl rubber. The ampoules were cooled with ice, and the aqueous and hydrocarbon phases containing the necessary components were introduced. The aqueous phase was a 3 % solution of potassium "paraffinate", and the hydrocarbon phase was ethylbenzene or a mixture of ethylbenzene and styrene (1 : 1). The ratio of hydrocarbon to aqueous phase was 1 : 2. The ethylenediamine amounted to 1 % by weight on the hydrocarbons. The hydroperoxide amounted to 0.5 % on the hydrocarbons. The concentration of iron salt and the order of mixing the components of the system was varied. The last component to be added (ethylenediamine, the hydroperoxide, or the iron salt) was sprayed in after the establishment of a stable emulsion. The moment at which this was done was taken as the start of the process.

The kinetics of the reaction were followed by observing the changes in hydroperoxide content. The contents of the ampoule were poured into a flask having a ground stopper; 50 ml of glacial acetic acid and 1.5 ml of saturated potassium iodide solution were added. The flask was closed, the stopper being moistened with KI solution; it was shaken for 40 minutes. The contents were then diluted with 100 ml of water, and the hydroperoxide content was determined by titration with thiosulfate. In order to determine the yield of polymer, the emulsion was broken, the hydrocarbon layer was separated in a separating funnel, and polystyrene was isolated from it with the aid of methanol. The polymer was washed with alcohol and dried to constant weight.

The copolymerization of butadiene and styrene was carried out similarly.

For the determination of α,α-dimethylbenzyl alcohol and acetophenone, 400 ml of the reaction mixture obtained when the whole of the hydroperoxide had been used up was extracted three times with cumene (total amount of cumene 120-150 ml). The main mass of cumene was then vacuum-distilled off at not above 40° and acetophenone and α,α-dimethylbenzyl alcohol were determined in the residue (about 30 g) by a known method [17, 18].

SUMMARY

1. A study was made of the kinetics of reaction between ethylenediamine and cumene hydroperoxide in aqueous and aqueous-hydrocarbon media in presence of various amounts of iron salts. It was shown that there is no direct relation between the kinetics of the decomposition of the hydroperoxide and the kinetics of polymerization. It was shown that the initiation of polymerization is not directly related to the oxidation-reduction reactions and that polymerization continues after the complete decomposition of the hydroperoxide.

2. The composition of the decomposition products of the hydroperoxide was studied. The mechanism of the action of the system was examined in the light of the results obtained.

LITERATURE CITED

[1] G. S. Whitby, N. Wellmann, V. W. Floutz and H. L. Stephens, Ind. Eng. Chem. 42, 3, 445 (1950).

[2] R. Spolsky and H. L. Williams, Ind. Eng. Chem. 42, 9, 1847 (1950).

[3] W. H. Embry, R. Spolsky and H. L. Williams, Ind. Eng. Chem. 43, 11, 2553 (1951).

[4] W. Kern, Macromol. Chem. 1, 209 (1948); 2, 249 (1948).

[5] B. A. Dolgoplosk and D. Sh. Korotkina, J. Appl. Chem. (in the press: No. 3, 1958).*

[6] R. I. Orr, and H. L. Williams, Disc. Faraday Soc. 14, 171 (1953).

[7] R. I. Orr and H. L. Williams, J. Am. Chem. Soc. 76, 12, 3321 (1954).

[8] L. Horner, Ang. Chem. 62, 359 (1951).

[9] S. P. Gambarian, Ber. 42, 4003 (1909); 58, 1775 (1925).

[10] S. P. Gambarin and A. O. Chaltykian, Ber. 60, 390 (1927).

[11] S. P. Gambarian and L. Kazarin, J. Gen. Chem. 3, 222 (1933).

[12] A. O. Chaltykian, Questions of Kinetics and Reactivity, 1955, p. 354.**

* See C. B. Translation.

** In Russian.

[13] L. Horner, and E. Schlenk, Ang. Chem. 61, 411 (1949).

[14] V. Ia. Andakushkin, B. A. Dolgoplosk, and I. I. Radchenko, J. Gen. Chem. 26, 2972 (1956).*

[15] M. S. Kharasch, A. Fono and W. Nudenberg, J. Org. Chem. 16, 1, 113 (1951).

[16] G. P. Belonovskaia, B. A. Dolgoplosk, and E. I. Tiniakova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 12, 1478 (1956).*

[17] V. F. Polikarpova, All-Union Synthetic Rubber Research Institute Specification No. 9516 (1954).

[18] V. F. Polikarpova and A. I. Kaganova, Addenda to All-Union Synthetic Rubber Research Institute Specification No. 9516 (1954).

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HYDROLYSIS OF POLYHALOHYDROCARBONS CONTAINING THE $CHal_3$ OR $CCl_2{=}CH$ GROUP

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The hydrolysis of trichloromethyl and dichlorovinyl groups can be effected with hot concentrated sulfuric acid; in some cases the use of oleum makes it possible to carry out the reaction at room temperature [1]. However, this method of hydrolysis has severe limitations. Thus, in the hydrolysis of higher $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes with concentrated sulfuric acid considerable resinification occurs and the yields of 13-chlorotridecanoic and 15-chloropentadecanoic acids are only 42 % and 24 % respectively. The method is not applicable [2] for the preparation of α-chloro carboxylic acids by the hydrolysis of compounds containing the $CCl_3{-}CHCl$ group. In the hydrolysis of polychlorohydrocarbons containing an aromatic ring, in some cases sulfonation of the nucleus is observed [3].

As the authors of the present paper have shown [4], in the treatment of saturated polychlorohydrocarbons of structure $Cl(CH_2)_n CCl_3$ (n is 4, 6, 8, or 10) and $Cl(CH_2)_3CHClCCl_3$, with fuming nitric acid, hydrolysis of trichloromethyl to carboxyl again occurs. The action of nitric acid on compounds containing the $CCl_2{=}CH$ group is complicated and gives several products [5].

In the present investigation we continued work on the action of nitric and perchloric acid in the hydrolysis of polyhalohydrocarbons. We showed that concentrated nitric acid can be used for the hydrolysis of the CCl_3 group of higher polychlorohydrocarbons. In this case hydrolysis is effected only by fuming nitric acid, sp.gr. 1.51--1.52. Reaction begins at room temperature or with slight warming (about 40°), but to complete reaction the mixture must be heated for 2-2.5 hours at 70-75°. Thus, by the action of nitric acid on α,α,α-trichloroalkanes containing 13, 15, and 17 carbon atoms,* satisfactory yields of the corresponding carboxylic acid were obtained.

It should be noted that the yields of 9-chlorononanoic and 11-chloroundecanoic acid can be appreciably improved, as compared with those obtained previously [4], if the tetrachloroalkanes taken are pure (free from dehydrochlorination products) and the time of heating with concentrated nitric acid is reduced to 2-2.5 hours. It is interesting that the chlorine formed by the nitric acid oxidation of hydrogen chloride liberated in the hydrolysis of the CCl_3 group chlorinates the products only to a very slight extent. Thus, the hydrolysis of 1,1,1-trichloroheptane with nitric acid gave heptanoic acid in good yield, and after two distillations the product was quite free from chlorine.

In a previous investigation [4] we showed that compounds containing chlorine in the α-position to the trichloromethyl group are also readily hydrolyzed when heated with fuming nitric acid, though a higher temperature (120-125°) and a large excess of nitric acid are required. In the case of 1,2-dibromo-1,1,5-trichloropentane we found that hydrolysis of the CCl_2Br group with nitric acid proceeds extremely vigorously even at room temperature with formation of 2-bromo-5-chlorovaleric acid in 82% yield.

Neither sulfuric nor perchloric acid affects a CCl_2Br group having a vicinal halogen atom. Attempts to hydrolyze the CCl_2Br group of (2,3-dibromo-3,3-dichloro)benzene by means of nitric acid did not give satisfactory results, for hydrolysis of this group was accompanied by the nitration and halogenation of the aromatic nucleus.

We found, that, unlike sulfuric and nitric acids, perchloric acid (even as a 70 % aqueous solution) is able to convert CCl_3 and $CH{=}CCl_2$ groups into carboxyls. However, these changes require severe conditions and are

* These trichloroalkanes were prepared by telomerization of ethylene with chloroform, see [6].

accompanied by considerable resinification. Thus, the hydrolysis of polychloroalkanes with perchloric acid requires heating at 115-130° for three hours. Hydrolysis of aromatic compounds of this type must be carried out in an inert medium, such as acetic acid, because the direct action of perchloric acid results in complete resinification. Increase in the amount of perchloric acid up to a certain limit increases the yield of carboxylic acid to some extent. The CCl_3 group can still be hydrolyzed by 60 % perchloric acid, but the 60 % acid no longer reacts with the $CH{=}CCl_2$ group. The use of perchloric acid makes it possible to hydrolyze polyhalo compounds containing an aromatic nucleus without any substitution of the nucleus.

EXPERIMENTAL

1. Hydrolysis of 1,1,1-Trichloroheptane with Nitric Acid. A mixture of 55 g of 1,1,1-trichloroheptane and 80 ml of nitric acid sp.gr. 1.52 was stirred at room temperature for 45 minutes and was then heated, first for 45 minutes at 40° and then for 90 minutes at 55-60°. The reaction mixture was diluted with water, and the oil that separated was extracted with chloroform. The acid products were extracted from the chloroform layer by means of 10 % sodium hydroxide solution. The alkaline solution was acidified, and heptanoic acid was extracted with chloroform. Solvent was distilled off, and the residue was vacuum-distilled. The following fractions were obtained:

Fraction I, up to 94° (4 mm); 1.3 g; n_D^{20} 1.4248

Fraction II, b.p. 94-95° (4 mm); 26.6 g; n_D^{20} 1.4260

Fraction III, above 96° (4 mm); 3.4 g; n_D^{20} 1.4380

Redistillation of Fraction II gave 20.1 g (57 %) of pure heptanoic acid, free from chlorine; b.p. 94-95° (4 mm); n_D^{20} 1.4248; d_4^{20} 0.9231; found MR 36.05; calculated MR 36.06 and 4.8 g (13.6 %) of heptanoic acid containing traces of chlorine (Beilstein test); b.p. 95-96° (4 mm); n_D^{20} 1.4250; d_4^{20} 0.9257; found MR 35.85. For heptanoic acid the literature gives b.p. 120° (18 mm); $n_D^{18.8}$ 1.4255; $d_4^{18.8}$ 0.9212.

2. Hydrolysis of 1,1,1,9-Tetrachlorononane with Nitric Acid. When 50 g of 1,1,1,9-tetrachlorononane and 70 ml of nitric acid sp.gr. 1.52 were stirred together, evolution of heat and liberation of gas were observed; this continued for 30 minutes, and the mixture was then heated for two hours at 60-70°. The precipitated oil obtained by dilution of the reaction mixture with water was extracted with chloroform, and the extract was washed with water and dried over calcium chloride. Chloroform was distilled off; vacuum fractionation of the residue gave:

Fraction I, up to 140° (3 mm); 2.4 g; n_D^{20} 1.4609

Fraction II, b.p. 141-150° (3 mm); 29.0 g; n_D^{20} 1.4619

Redistillation of Fraction II gave 26.8 g (74 %) of 9-chlorononanoic acid, b.p. 136-140° (2 mm); n_D^{20} 1.4619; d_4^{20} 1.0614; found MR 49.80; calculated MR 50.16; yield 74 % of theoretical.

3. Hydrolysis of 1,1,1,11-Tetrachloroundecane with Nitric Acid. The hydrolysis of 15 g of 1,1,1,11-tetrachloroundecane was carried out as described above. Fractionation gave:

Fraction I, up to 155° (3 mm); 0.5 g; n_D^{20} 1.4580

Fraction II, b.p. 155-163° (3 mm); 1.0 g.

Fraction III, b.p. 165-168° (3 mm); 8.68 g

Fractions II and III solidified. Fraction III was 11-chloroundecanoic acid, obtained in 77 % yield. After being recrystallized from petroleum ether it melted at 38-39° (the literature [2] gives m.p. 41-42°). Titration with alkali showed that Fraction II contained 85 % of 11-chloroundecanoic acid.

4. Hydrolysis of 1,1,1-Trichlorotridecane with Nitric Acid. A mixture of 10.1 g of 1,1,1-trichlorotridecane and 25 ml of nitric acid sp.gr. 1.52 was prepared and, when evolution of heat ceased, it was heated for 2.5 hours at 85-90°. The reaction mixture was diluted with water and cooled; the organic layer solidified. Crystallization from acetone gave 4.68 g (61.6 %) of tridecanoic acid, m.p. 30-32°, raised to 39° by two recrystallizations from petroleum ether; it contained no chlorine. Data in the literature: m.p. 39° [8], 41° [9]. The anilide prepared from the acid had m.p. 78° (from methanol).

Found %: C 78.66; 78.70; H 10.65; 10.68 $C_{19}H_{31}ON$. Calculated %: C 78.83; H 10.79

5. Hydrolysis of 1,1,1-Trichloropentadecane with Nitric Acid. The hydrolysis of 10 g of 1,1,1-trichloropentadecane was carried out with 25 ml of nitric acid sp.gr. 1.52, as described in Experiment 2. The yield of crude pentadecanoic acid, m.p. 33-35°, was 7.41 g. When this was treated with cold acetone there remained 5.09 g (66.6 %) of the acid, m.p. 40-43°. After recrystallization from petroleum ether it melted at 51-52° and did not contain chlorine. The literature gives m.p. 50° [10], 52° [11]. The anilide prepared from the acid had m.p. 85°.

Found %: C 79.18; 79.25; H 11.17; 11.10. $C_{21}H_{35}ON$. Calculated %: C 79.43; H 11.11.

6. Hydrolysis of 1,1,1-Trichloroheptadecane with Nitric Acid. A mixture of 8.5 g of 1,1,1-trichloroheptadecane and 20 ml of nitric acid sp.gr. 1.52 was heated for three hours at 60-65°. The further procedure was as described in Experiment 4. Recrystallization from absolute alcohol gave 2.21 g of the acid, m.p. 45-50°. The mother liquor yielded a further 0.42 g of the acid, m.p. 56°. The total yield was 40%. Recrystallization from petroleum ether gave a product of m.p. 61°; it was free from chlorine. For heptadecanoic acid the literature gives m.p. 60-61° [12], 62° [13]. The anilide of heptadecanoic acid had m.p. 88°.

Found %: C 79.62; 79.50; H 11.54; 11.55; $C_{23}H_{39}ON$. Calculated %: C 79.94; H 11.37.

7. Hydrolysis of 1,2-Dibromo-1,1,5-trichloropentane with Nitric Acid. When 20 g of 1,2-dibromo-1,1,5--trichloropentane and 30 ml of nitric acid sp.gr. 1.52 were mixed, a very vigorous reaction set in (periodic cooling was necessary). The reaction mixture was then heated for 30 minutes at 55-60°. The product, amounting to 10.8 g (82 %), was 2-bromo-5-chlorovaleric acid, b.p. 136-137° (3 mm); n_D^{20} 1.5070; d_4^{20} 1.6317; found MR 39.30; calculated MR 39.45. The literature [14] gives b.p. 126° (2.5 mm); n_D^{20} 1.5068; d_4^{20} 1.6307.

8. Hydrolysis of 1,1,1,7-Tetrachloroheptane with Perchloric Acid. A mixture of 30 g of 1,1,1,7-tetrachloroheptane and 40 ml of 70 % perchloric acid was heated for two hours at 115-120°. The dark-colored reaction mixture was cooled and diluted with water. The further treatment was as described for Experiment 1. The product, amounting to 11.9 g (57 %), was 7-chloroheptanoic acid, b.p. 130-131° (4 mm); n_D^{20} 1.4580; d_4^{20} 1.1016; found MR 40.78; calculated MR 40.93. For 7-chloroheptanoic acid the literature [15] gives n_D^{25} 1.4550; d_4^{25} 1.0916.

9. Hydrolysis of 1,1,5-Trichloro-1-pentene with Perchloric Acid. A mixture of 20 g of 1,1,5-trichloro-1--pentene and 20 ml of 70 % perchloric acid was heated at 115-120° for two hours. The treatment described for Experiment 1 gave 8.8 g (56 %) of 5-chlorovaleric acid, b.p. 105-106° (3 mm); n_D^{20} 1.4569; d_4^{20} 1.1806; found MR 31.50; calculated MR 31.69. The literature [15] gives b.p. 122-124° (8 mm); n_D^{25} 1.4525; d_4^{25} 1.1667.

10. Hydrolysis of 1,1,7-Trichloro-1-heptene with Perchloric Acid. A mixture of 20 g of 1,1,7-trichloro-1-heptene and 25 ml of 70 % perchloric acid was heated at 125-130° for two hours. The treatment of Experiment 9 gave 8.9 g (64 %) of 7-chloroheptanoic acid, b.p. 123-125° (2 mm); n_D^{20} 1.4581; d_4^{20} 1.020.

11. Hydrolysis of (3,3-Dichloro-2-propenyl)benzene with Perchloric Acid. A mixture of 15 g of (3,3-dichloro-2-propenyl)benzene, 25 ml of perchloric acid, and 20 ml of glacial acetic acid was heated at 130° for four hours. Treatment as described for Experiment 1 gave 3.0 g (25 %; 46 % on the amount of chloro compound that reacted) of hydrocinnamic acid, b.p. 127-128° (3 mm). When cooled slightly the hydrocinnamic acid that had distilled over solidified. After being recrystallized from water it melted at 46-46.5°. In admixture with a known sample of hydrocinnamic acid there was no depression of melting point. The chloroform solution yielded 6.9 g of unchanged (3,3-dichloro-2-propenyl)benzene, b.p. 85° (4 mm) and n_D^{20} 1.5499.

SUMMARY

1. Some α,α,α-trichloro- and α,α,α,ω-tetrachloro-alkanes were hydrolyzed by means of hot nitric acid of sp.gr. 1.51-1.52.

2. It was shown that the higher trichloro- and tetrachloro-alkanes (11, 13, 15, and 17 carbon atoms) are smoothly hydrolyzed with formation of the corresponding carboxylic and ω-chloro carboxylic acids (having the same number of carbon atoms in their molecules).

3. The hydrolysis of aliphatic compounds containing the $CHBr{-}CCl_2Br$ group by nitric acid of sp.gr. 1.52 proceeds at room temperature with formation of the corresponding α-bromo carboxylic acids in high yield. Neither concentrated sulfuric nor 70% perchloric acid hydrolyzes compounds of this structure.

4. Perchloric acid (70 %) hydrolyzes both aliphatic and aromatic compounds containing the CCl_3 or $CCl_2{=}CH$

group with formation of the corresponding carboxylic acids. Reaction requires comparatively severe conditions (115-130°), and it is accompanied by considerable resinification.

LITERATURE CITED

[1] A. Roedig and E. Degeuer, Ber. 86, 1469 (1953).

[2] A. N. Nesmeianov and L. I. Zakharkin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 224.*

[3] A. N. Nesmeianov, R. Kh. Freidlina and N. A. Semenov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 993.*

[4] R. Kh. Freidlina and E. I. Vasil'eva, Proc. Acad. Sci. USSR 100, No. 1, 85.

[5] L. I. Zakharkin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1064.*

[6] A. N. Nesmeianov, Sh. A. Kareptian, and R. Kh. Freidlina, Proc. Acad. Sci. USSR 109, No. 4, 791 (1956).*

[7] A. Vogel, J. Chem. Soc. 1929, 729.

[8] S. Posternak, C. r. 162, 946 (1916).

[9] M. Bougault, and C. Charaux, C. r. 153, 881 (1911).

[10] S. Skraup and E. Schwamberger, Ann. 462, 155 (1928).

[11] R. Majima and J. Nakamura, Ber. 46, 4095 (1913).

[12] H. le Sueur, J. Chem. Sco. 85, 836 (1904).

[13] F. Francis, S. Piper and T. Malkin, Proc. Ray. Soc. (A), 128, 217 (1930).

[14] A. N. Nesmeianov, R. Kh. Freidlina, and R. G. Petrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 451.*

[15] R. Joyce, W. Hanford and J. Harmon, J. Am. Chem. Soc. 70, 2529 (1948).

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SYNTHESIS AND PROPERTIES OF TRICHLOROMETHYL- AND 3,3-DICHLOROALLYL MERCURY COMPOUNDS

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In recent years we have studied the chemical transformations of trichloromethyl and 2,2-dichlorovinyl groups in polychlorohydrocarbons and related compounds,* and we considered it to be of interest to find methods of synthesis of organomercury compounds containing these groups and to study their properties. In particular, these compounds could be used for the preparation of other heteroorganic compounds of this type. It is of interest also to study the properties of the $CCl_3^{\cdot}$ and $CCl_2{=}CHCH_2^{\cdot}$ radicals generated by the decomposition of organomercury compounds of this structure (cf., e.g., [2]).

It should be noted that, although organomercury compounds containing the trifluoromethyl group have been prepared [3], attempts to synthesize the trichloromethyl compounds have not been successful. Thus, by the thermal decarboxylation of mercuric trichloroacetate Kharasch and Staveley [4] obtained calomel instead of the expected bistrichloromethylmercury. An attempt to prepare trichloromethylmercury chloride from carbon tetrachloride and mercury under ultraviolet irradiation was also unsuccessful [5].

Trifluoromethylmercury halides and bistrifluoromethylmercury, which were synthesized by Emeleus and Haszeldine [3], approach inorganic salts of mercury in some of their properties: they are soluble in water, and their aqueous solutions conduct electricity. When treated with the usual symmetrizing agents (KI, Na/Hg, $Na_2S_2O_3$), trifluoromethylmercury halides do not give bistrifluoromethylmercury, but are decomposed with formation of fluoroform. Trifluoromethylmercury compounds, like $HgCl_2$, appear to be able to add at a double bond. Thus, Haszeldine [6] noted that ultraviolet irradiation of a mixture of CF_3I and C_2H_4 at 180° in presence of mercury gives $CF_3CH_2CH_2HgI$, though in very low yield.

As yet, no 3,3-dihaloallylmercury compound has been described in the literature.

Vigorous agitation of a mixture of CCl_3Br and mercury under the irradiation of a PRK-4 mercury lamp in the cold, though better at 70-80°, gave trichloromethylmercury bromide in 41 % yield. Addition of a little 2,2'-azobis[2-methylpropionitrile] to the reaction mixture increased the yield of CCl_3HgBr. Without irradiation reaction did not go at room temperature and gave only a 7.3 % yield of CCl_3HgBr at 70-80° in presence of the azo dinitrile. However, when the reaction was carried out in a quartz test tube with simultaneous irradiation, heating, and addition of catalyst, the amount of by-product polymeric and inorganic mercury compounds formed was greatly increased and the yield of trichloromethylmercury bromide was affected unfavorably.

Treatment of CCl_3HgBr with moist silver oxide gave trichloromethylmercury hydroxide. When an alcoholic solution of this compound was acidified with 2 N HCl or HI and then diluted with water, CCl_3HgCl or CCl_3HgI** were precipitated. The precipitation of CCl_3HgCl was incomplete owing to the appreciable solubility of this compound in water. CCl_3HgCl and CCl_3HgBr are quite stable and do not decompose with keeping; CCl_3HgI gradually decomposes with formation of HgI_2, particularly in the light. Trichloromethylmercury halides give complexes with pyridine. In the case of CCl_3HgI the pyridine complex is unstable and rapidly decomposes with keeping.

Reaction between CCl_3HgBr and $(C_6H_5)_2SnCl_2$ takes various courses according to the amount of alkali taken

* For a review of these investigations see [1].

** CCl_3HgI can be prepared also by simply shaking CCl_3I with mercury in the cold, in spite of Besson's assertion [7], namely, that CCl_3I is completely decomposed by mercury in the course of a few hours with liberation of I_2 and formation of C_2Cl_6.

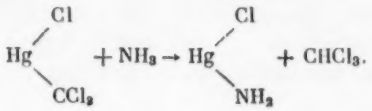
for reaction. When the relative amounts of reactants were stoichiometric in accordance with Equation (1), we obtained phenyl(trichloromethyl)mercury:

$$2CCl_3HgBr + (C_6H_5)_2SnCl_2 + 6NaOH \rightarrow 2C_6H_5HgCCl_3 + \\ + Na_2SnO_3 + 2NaCl + 2NaBr + 3H_2O; \quad (1)$$

With a 100% excess of alkali, diphenylmercury was obtained. With methanolic HCl, phenyl(trichloromethyl)mercury gave C_6H_5HgCl in quantitative yield, which indicates that the electronegativity of the trichloromethyl group is greater than that of the phenyl group.

An attempt to synthesize phenyl(trichloromethyl)mercury by the photochemical decarboxylation of $C_6H_5HgOCOCCl_3$ was not successful. After ultraviolet irradiation of methanolic $C_6H_5HgOCOCCl_3$ for eight hours, phenylmercury chloride and unchanged $C_6H_5HgOCOCCl_3$ were isolated from the reaction mixture.

Treatment of a chloroform solution of CCl_3HgCl with dry ammonia did not give bistrichloromethylmercury; all the mercury came out of solution in the form of infusible precipitate:

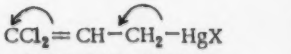


(2)

Even in the cold, mercuric sulfide was precipitated quantitatively when alcoholic solutions of CCl_3HgBr were treated with hydrogen sulfide. Reaction between CCl_3HgBr and $AgNO_3$ was almost instantaneous in slightly warm alcoholic solution, all the bromine present in the CCl_3HgBr being precipitated as AgBr by Ag^+. The trichloromethyl group does not remain inert to $AgNO_3$, and yields all its chlorine in presence of excess of the reagent. Excess of silver oxide acts similarly on trichloromethylmercury bromide. Treatment of trichloromethylmercury halides with the usual symmetrizing agents (KI, $Na_2S_2O_3$, Cu) does not give bistrichloromethylmercury.

These facts differentiate trichloromethylmercury compounds from the usual organomercury compounds and indicate their resemblance to inorganic salts of mercury. It is known that pyridine complexes are formed by only a few organomercury compounds of salt-like character, namely quasicomplex compounds [8, 9] and some others (see e.g. [10]). Finally, the reactions of trichloromethylmercury halides with NH_3 and H_2S are highly reminiscent of similar reactions of mercuric chloride. Comparison of trichloromethylmercury compounds with their fluorine analogs indicates that the CCl_3 group is less stable than CF_3.

3,3-Dichloroallylmercury iodide was prepared by direct reaction of $CCl_2{=}CHCH_2I$ with mercury. At room temperature without irradiation reaction was rather slow and yields did not exceed 44 %. In a wide-mouthed quartz test tube with irradiation by a PRK-4 mercury lamp, reaction was complete within 30 minutes and the yield of $CCl_2{=}CHCH_2HgI$ was 67 %. This product is unstable and decomposes on keeping with separation of HgI_2. Treatment of an alcoholic solution of 3,3-dichloroallylmercury iodide with moist silver oxide and subsequent treatment with 2 N HCl or 2 N HBr gave $CCl_2{=}CHCH_2HgBr$ or $CCl_2{=}CHCH_2HgCl$.

Neither $CCl_2{=}CHCH_2HgI$ nor $CCl_2{=}CHCH_2HgCl$ behaves as a conjugated system  (see e.g. [11]) in reaction with maleic anhydride. These compounds do not react with benzoyl chloride with formation of ketones. When $CCl_2{=}CHCH_2HgI$ was treated with C_6H_5COCl, no ketone was formed; a resinous reaction mixture was obtained, and from this, by chromatography on alumina, we isolated $CCl_2{=}CHCH_2HgCl$, HgI_2, $HgCl_2$, and unchanged $CCl_2{=}CHCH_2HgI$ and C_6H_5COCl. In this reaction the behavior of $CCl_2{=}CHCH_2HgI$ is reminiscent of that of its allyl analog [12].

EXPERIMENTAL

1,1-Dichloro-3-iodopropene. To a solution of 30 g (0.2 mole) of NaI in 150 ml of acetone, 30 g (0.2 mole) of $CCl_3CH{=}CH_2$ was added and the mixture was boiled in a water bath for 90 minutes. The reaction product was then poured into water, and the lower layer was separated, washed with sodium thiosulfate solution and with water, dried over sodium sulfate, and vacuum-distilled. A fraction of b.p. 68-70° (10 mm) (19.7 g) was collected. Redistillation gave 15.2 g (34 %) of $CCl_2{=}CHCH_2I$*, b.p. 63° (8 mm); n_D^{20} 1.6020; d_4^{20} 2.0320. 1,1-Dichloro-

* Compare [13].

-3-iodopropene is very unstable and decomposes even during distillation.

Found %: C 15.29; 15.20; H 1.39; 1.57; Cl 30.45; 30.42. $C_3H_3Cl_2I$. Calculated %: C 15.21; H 1.28; Cl 29.94.

3,3-Dichloroallylmercury Iodide. A mixture of 6 g of $CCl_2{=}CHCH_2I$ and 50 g of mercury was agitated vigorously for 30 minutes in a wide-mouthed quartz test tube, which was irradiated with a PRK-4 mercury lamp (current 4 amp) placed at a distance of 15 cm. The reaction mixture was then extracted with chloroform in a Soxhlet. Evaporation of the chloroform left 7.4 g (67 %) of $CCl_2{=}CHCH_2HgI$, m.p. 46° after two recrystallizations from chloroform. 3,3-Dichloroallylmercury iodide forms slightly yellowish needles which turn red rapidly when exposed to light.

Found %: C 8.80; 8.85; H 0.72; 0.64; Cl 16.97; 17.04. $C_3H_3Cl_2IHg$. Calculated %: C 8.23; H 0.69; Cl 16.20.

3,3-Dichloroallylmercury Chloride. $CCl_2{=}CHCH_2HgI$ (23 g) was dissolved in 100 ml of hot alcohol, and Ag_2O prepared from 18 g of $AgNO_3$ was added. The mixture was boiled with continuous stirring fro 20 minutes, and the precipitate was then filtered off. A solution of 13 g of NaCl in 100 ml of water was added to the cooled filtrate, and the mixture was acidified to phenolphthalein with 2 N HCl. After 12 hours the precipitate of $CCl_2{=}CHCH_2HgCl$ was filtered off and vacuum-dried; yield 13 g (71.5 %). After recrystallization from chloroform 3,3-dichloroallylmercury chloride was obtained in silky needles, m.p. 100°, readily soluble in ether and acetone, moderately soluble in ethanol.

Found %: C 10.17; 10.39; H 0.94; 1.13. $C_3H_3Cl_3Hg$. Calculated %: C 10.41; H 0.87.

When an attempt was made to prepare a pyridine complex from $CCl_2{=}CHCH_2HgCl$ in a benzene medium, the original compound was recovered quantitatively.

3,3-Dichloroallylmercury Bromide. 3,3-Dichloroallylmercury bromide was prepared, like $CCl_2{=}CHCH_2HgCl$, from 4.4 g of $CCl_2{=}CHCH_2HgI$ (70 % yield). After being recrystallized twice from alcohol $CCl_2{=}CHCH_2HgBr$ melted at 93-94.5°.

Found %: C 8.67; 8.73; H 0.73; 0.77. $C_3H_3Cl_2BrHg$. Calculated %: C 9.23; H 0.77.

Trichloromethylmercury Bromide. A mixture of 7.5 g (0.037 mole) of CCl_3Br, 80 g (0.4 g-atom) of mercury, and 0.01 g of 2,2'-azobis[2-methylpropionitrile] was prepared in a glass test tube, about 4 cm in diameter; this was connected on the outside with a thermometer and was fitted with a rapid centrifugal stirrer. The mixture was heated in an air bath at 70-80° for three hours with continuous shaking and irradiation with a PRK-4 mercury lamp (current 4 amp) at a distance of 15 cm. The reaction mixture was then extracted with three 50-ml portions of boiling acetone, and the acetone extracts were evaporated at room temperature until a slurry formed; this was treated with 10-20 ml of cold chloroform. The resulting precipitate was filtered off. The yield of CCl_3HgBr was 6.2 g (41 %). After being recrystallized from chloroform, trichloromethylmercury bromide was obtained as colorless silky needles, m.p. 165°, readily soluble in acetone, less readily in ether, benzene, and boiling chloroform.

Found %: C 3.10; 3.25; Cl 26.78; 26.69; Br 20.03; 20.23. CCl_3HgBr. Calculated %: C 3.03; Cl 26.68; Br 20.03.

Pyridine Complex of Trichloromethylmercury Bromide. Pyridine (1 ml) was added to a solution of 0.5 g of CCl_3HgBr in 5 ml of benzene, and the resulting mixture was evaporated at room temperature in a stream of air until the volume was reduced to 1 ml. The residue was treated with water, and the precipitate formed was extracted with ether; ether was then evaporated, and the complex was recrystallized from benzene; yield 0.4 g (67 %). The complex was obtained as a yellowish finely crystalline powder melting with decomposition at 87°; according to analysis it contains one molecule of pyridine.

Found %: C 15.15; 14.91; H 0.87; 0.81; Cl 22.08; 22.00; Br 16.57; 16.55. $CCl_3HgBr \cdot C_5H_5N$. Calculated %: C 15.07; H 1.05; Cl 22.25; Br 16.72.

Trichloromethylmercury Hydroxide. A solution of 0.8 g of CCl_3HgBr in 10 ml of alcohol was mixed with a suspension of Ag_2O (from 0.4 g of $AgNO_3$) in 5 ml of alcohol, and the mixture was boiled for 15 minutes with continuous stirring. The precipitate was filtered off, and the filtrate was evaporated under reduced pressure to the consistency of a sirup. Treatment of the sirup with petroleum ether gave a crystalline precipitate of CCl_3HgOH;

yield 0.55 g (75 %). After being recrystallized from chloroform, trichloromethylmercury hydroxide melted with decomposition at 175° in a sealed capillary. When left in the air it rapidly absorbed CO_2.

Found %: C 3.91; 4.00; H 0.02; 0.05; Cl 31.66. CCl_3HgOH. Calculated %: C 3.57; H 0.30; Cl 31.65.

Trichloromethylmercury Chloride. The solution of trichloromethylmercury hydroxide obtained from 0.8 g of CCl_3HgBr as described in the previous experiment was acidified with 2 N HCl (to Methyl orange with a slight excess) and poured into 50 ml of water. The precipitate of trichloromethylmercury chloride (0.4 g) was filtered off. Extraction of the filtrate with ether gave a further 0.1 g of CCl_3HgCl. The total yield was 0.5 g (70 % on the CCl_3HgBr taken). Trichloromethylmercury chloride formed fine white needles melting with decomposition at 173°; it was similar to CCl_3HgBr in properties.

Found %: C 3.29; 3.16; Hg 56.90; 56.87. CCl_4Hg. Calculated %: C 3.39; Hg 56.60.

Trichloromethylmercury Iodide. CCl_3HgI was prepared like CCl_3HgCl from 0.8 g of trichloromethylmercury bromide; yield 0.5 g (56 %). It forms plates with a pearly sheen, m.p. 116-117° with decomposition; it reddens when exposed to light.

Found %: Cl 23.42; 23.92. CCl_3HgI. Calculated %: Cl 23.85.

Trichloromethylmercury iodide was prepared also by gradual addition of 2.8 g of CCl_3I[b.p. 52° (68 mm)] to 50 g of mercury with shaking and cooling and subsequent extraction of the reaction mixture with boiling chloroform in a Soxhlet for 30 minutes. Yield of CCl_3HgI 3 g (56 %); m.p. 117° (with decomposition).

Found %: C 2.85; 2.93. CCl_3HgI. Calculated %: C 2.69.

Reaction of Trichloromethylmercury Bromide with Dichlorodiphenylstannane. a) A solution of 0.66 g (0.0165 mole) of NaOH in 10 ml of alcohol was added to a boiling solution of 2.2 g (0.0055 mole) of CCl_3HgBr and 1.0 g (0.0029 mole) of $(C_6H_5)_2SnCl_2$ in 30 ml of ethanol. The solution was filtered hot, cooled with a mixture of ice and salt, and diluted with an equal amount of water. The precipitate of $CCl_3HgC_6H_5$ was collected and dried; yield 0.5 g (23 %), m.p. 126-127.5° (from alcohol).

Found %: C 21.73; 21.75; H 1.58; 1.70. $C_7H_5HgCl_3$. Calculated %: C 21.23; H 1.24.

When 2 ml of 2 N methanolic HCl was added to 0.03 g of $CCl_3HgC_6H_5$ in 2 ml of methanol, 0.02 g (84 %) of C_6H_5HgCl, m.p. 251-253°, was obtained.

b) CCl_3HgBr (1.86 g) and $(C_6H_5)_2SnCl_2$ (0.8 g) were treated with 0.80 g of NaOH in the way described above; the filtrate was diluted with an equal amount of water and left for one hour in the cold, after which the precipitate of diphenylmercury (0.45 g, i.e. 49 % yield) was filtered off and recrystallized from alcohol; m.p. 124-124.5°, undepressed by admixture of a known sample. No mercury was detected in the filtrate.

Phenylmercury Trichloroacetate. A hot alcoholic solution of C_6H_5HgOH (obtained from 6 g of C_6H_5HgCl by shaking it with Ag_2O) was diluted with aqueous CCl_3COOH until reaction to Methyl orange was acid. On dilution of the solution with water, phenylmercury trichloroacetate separated and was filtered off and vacuum-dried; yield 6.9 g (78 %). After being recrystallized from aqueous methanol the phenylmercury trichloroacetate melted with decomposition at 238-240°.

Found %: C 21.46; 21.43; H 1.10; 1.27; Hg 45.52; 46.05. $C_8H_5O_2HgCl_3$. Calculated %: C 21.60; H 1.15; Hg 45.35.

Photochemical Decomposition of Phenylmercury Trichloroacetate. A solution of 3 g of $C_6H_5HgOCOCCl_3$ in 40 ml of methanol was irradiated for eight hours with a PRK-4 mercury lamp (current 4 amp) at a distance of 15 cm; temperature 30-35°. The precipitate formed (1.14 g, i.e. 94 % yield on the $C_6H_5HgOCOCCl_3$ that reacted) was filtered off and dried. After recrystallization from alcohol it had m.p. 251°, undepressed by admixture of known C_6H_5HgCl. When the filtrate was evaporated to dryness, 1.30 g of $C_6H_5HgOCOCCl_3$; was recovered (m.p. 237-239° with decomposition).

Reaction of CCl_3HgCl with Ammonia. Dry ammonia was passed for ten minutes through a solution of 1.20 g of CCl_3HgCl in 20 ml of chloroform. A flocculent precipitate began to form immediately. The reaction mixture was left overnight, and the precipitate of $ClHgNH_2$ was then filtered off and washed with cold water, alcohol, and boiling ether. Evaporation of the wash water did not give NH_4Cl. The weight of air-dried precipitate was 0.81 g [95.5 % as calculated from Equation (2)].

Found %: N 6.15; 6.30. NH_2HgCl. Calculated %: N 5.56.

Reaction of CCl_3HgBr with Hydrogen Sulfide. Hydrogen sulfide was passed for 30 minutes through a solution of 1.10 g of CCl_3HgBr in 15 ml of ethanol. The resulting precipitate of mercuric sulfide was filtered off, washed with alcohol and carbon disulfide, and vacuum-dried at 60°. The weight of dried HgS was 0.63 g (98.7 %).

SUMMARY

1. Trichloromethylmercury bromide was synthesized by reaction between mercury and bromotrichloromethane in presence of radiation; the product was converted by the usual methods into trichloromethylmercury hydroxide, chloride, and iodide.

2. Phenyl(trichloromethyl)mercury was synthesized by reaction of trichloromethylmercury bromide with dichlorodiphenyltin in an alkaline medium. Reaction of the product with hydrogen chloride gave phenylmercury chloride, which indicates the high electronegativity of the trichloromethyl group, as compared with that of the phenyl group.

3. Trichloromethylmercury halides form complex compounds with pyridine. The double compound of pyridine with trichloromethylmercury bromide survives recrystallization and has the composition $CCl_3HgBr \cdot C_5H_5N$.

4. The complex-formers ammonia and hydrogen sulfide completely destroy trichloromethylmercury halides.

5. 3,3-Dichloroallylmercury iodide was synthesized by reaction between 1,1-dichloro-3-iodopropene and mercury in presence of ultraviolet radiation; the product was converted by the usual methods into 3,3-dichloroallylmercury chloride and bromide.

LITERATURE CITED

[1] A. N. Nesmeianov, R. Kh. Freidlina, and L. I. Zakharkin, Prog. Chem. 25, 665, (1956).

[2] Iu. A. Ol'dekop, Doctorate thesis, Inst. Org. Chem. , Moscow, 1956.

[3] H. J. Emeleus, and R. N. Haszeldine, J. Chem. Soc. 1949, 2948, 2953.

[4] M. S. Kharasch and F. W. Staveley, J. Am. Chem. Soc. 45, 2961 (1923).

[5] A. N. Nesmeianov and O. A. Reutov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 655.*

[6] R. N. Haszeldine, J. Chem. Soc. 1949, 2856.

[7] A. Besson, Bull. (3) 9, 174 (1893); C.r. 115, 1078 (1892).

[8] R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1942, 14.

[9] A. N. Nesmeianov, R. Kh. Freidlina and A. E. Borisov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, 146.

[10] G. Vanags and V. Vitols, Kim. Inst. Zinatnisk. Raksti, Latvijas, RSP Zinatnu Akad. I, 97, 1950; C. A. 48, 5080 (1954).

[11] K. Alder and H. Soll, Ann. 565, 57 (1949); K. Alder, F. Pascher and A. Smitz, Ber. 76, 27 (1948).

[12] A. Oppenheim, Ber. 4, 669 (1871).

[13] A. N. Nesmeianov, L. I. Zakharkin, V. N. Kost and R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 258.*

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SOME REACTIONS OF THE AMINO GROUP OF 1,1,1-TRIETHYLSILYLAMINE

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Aminosilanes, compounds in which one or more valences of the silicon atom are attached to amino groups, have acquired great practical importance as active hydrophobizing agents. Data in the literature on the chemical properties of these compounds are nevertheless extremely limited. In the present investigation we studied some reactions of a silicon-attached amino group, the compounds examined being 1,1,1-triethylsilylamine and its N--methyl and -ethyl derivatives.

The preparation of 1,1,1-triethylsilylamine by the action of liquid ammonia on chlorotriethylsilane has been described [1, 2] (the analogous reaction with chlorotrimethylsilane gives hexamethyldisilazane [2, 3]). Some N--alkyl derivatives of 1,1,1-triethylsilylamine were obtained by reaction of triethylsilane with the corresponding amine in presence of alkali-metal amides [4] or metallic lithium [5]. N-Alkyl triethyl- and trimethyl-silylamines have been synthesized by the action of the corresponding amine on chlorotriethyl- and chlorotrimethyl-silanes [2, 6].

1,1,1-Triethylsilylamine reacts readily with hydrogen chloride or bromide, hydrochloric or hydrofluoric acid, or a mixture of hydrobromic and sulfuric acids with formation of triethylhalosilane [1]. N,1,1,1-Tetramethylsilylamine readily reacts with hydrogen chloride with formation of chlorotrimethylsilane and methylamine hydrochloride [2], and it reacts equally readily (in the cold) with chlorotrimethylsilane with formation of 1,1,1,2,3,3,3--heptamethyldisilazane [2]. N-Alkyl derivatives of 1,1,1-trimethylsilylamine are readily hydrolyzed in presence of acid or alkali with formation of trimethylsilanol [2].

1,1,1-Triethylsilylamine, its N-ethyl derivatives, and its previously undescribed N-methyl derivatives were prepared by reaction between chlorotriethylsilane and ammonia or the corresponding amine. Table 1 gives the physical properties of the compounds synthesized.

TABLE 1

Properties of 1,1,1-Triethylsilylamine and its N-Alkyl Derivatives

No.	Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	*MR*	
					Found	Calculated
1	$(C_2H_5)_3\ SiNH_2$	137 (751)	1.4275	0.7982	42.05	42.02
2	$(C_2H_5)_3\ SiNHCH_3$	151—153 (770)	1.4295	0.8011	47.02	47.02
3	$(C_2H_5)_3\ SiN\ (CH_3)_2$	166—167 (770)	1.4325	0.8044	51.33	51.63
4	$(C_2H_5)_3\ SiNHC_2H_5$	166—167 (745)	1.4300	0.7995	51.37	51.65
5	$(C_2H_5)_3\ SiN\ (C_2H_5)_2$	199.5—201 (755)	1.4400	0.8167	60.40	60.89

It was found that the compounds obtained have fairly high thermal stability. Thus, after seven hours at the boil 1,1,1-triethylsilylamine remained unchanged, and after 53 hours only 9 % was converted into the condensation product, hexaethyldisilazane. After being heated for 25 hours, N,N,1,1,1-pentaethylsilylamine was decomposed to the extent of 14 %.

1,1,1-Triethylsilylamine reacted with chlorotriethylsilane with great difficulty at room temperature and

somewhat more rapidly at the boil. After 16 hours at the boil the yield of hexaethyldisilazane, according to the equation

$$3(C_2H_5)_3SiNH_2 + (C_2H_5)_3SiCl \rightarrow 2[(C_2H_5)_3Si]_2NH + NH_4Cl$$

attained a maximum of 79 %, whereas in an experiment without heating only 30 % of the hexaethyldisilazane was obtained after 94 hours. It was stated above that for N,1,1,1-tetramethylsilylamine the analogous reaction proceeds quantitatively at room temperature. It may be supposed, therefore, that the stability of the Si—N bond in this reaction depends more on the chain lengths of the organic radicals attached to silicon than on the presence or chain length of substituents in the amino group.

1,1,1-Triethylsilylamine and its N-alkyl derivatives react with water with formation of triethylsilanol in 70-80 % yield:

$$(C_2H_5)_3SiNR_2 + H_2O \rightarrow (C_2H_5)_3SiOH + R_2NH,$$

(R = H, CH_3, C_2H_5).

The stability of the Si—N bond to hydrolysis increases with increase in the size and number of organic radicals attached to the nitrogen. Thus, whereas for 1,1,1-triethylsilylamine hydrolysis proceeds rapidly in a heterogeneous medium (ether as solvent) with appreciable evolution of heat, for its N-methyl and -ethyl derivatives the process is much less vigorous: under these conditions N,N,1,1,1-pentaethylsilylamine does not react at all with water, and it can be hydrolyzed only in a homogeneous medium [introduction of a common solvent (acetone)].

1,1,1-Triethylsilylamine reacts readily in the cold with aliphatic alcohols with formation of the corresponding alkoxytriethylsilanes:

$$(C_2H_5)_3SiNH_2 + ROH \rightarrow (C_2H_5)_3SiOR + NH_3.$$

TABLE 2

Properties of Alkoxytriethylsilanes

No.	Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	*MR*	
					Found	Calculated
1	$(C_2H_5)_3SiOC_2H_5$	152—153 (755)	1.4165	0.8165	49.12	49.37
2	$(C_2H_5)_3SiO$—*n*-C_3H_7	171.5—172 (753)	1.4210	0.8183	53.92	53.99
3	$(C_2H_5)_3SiO$—*i*-C_3H_7	157—158 (762)	1.4220	0.8237	53.68	53.99
4	$(C_2H_5)_3SiO$—*n*-C_4H_9	191—191.5 (754)	1.4225	0.8184	58.47	58.63
5	$(C_2H_5)_3SiO$—*i*-C_4H_9	182—183 (756)	1.4195	0.8131	58.49	58.63
6	$(C_2H_5)_3SiO$—*i*-C_5H_{11}	201—203 (759)	1.4240	0.8187	63.01	63.26
7	$(C_2H_5)_3SiO$—*n*-C_8H_{17}	115—116 (3)	1.4355	0.8263	77.13	77.15

Table 2 gives the properties of ethoxytriethylsilane prepared by us in this way, and it lists also the following new compounds: propoxy-, isopropoxy-, butoxy-, isobutoxy-, isopentyloxy-, and octyloxy-triethylsilanes. N--Methyl and -ethyl derivatives of 1,1,1-triethylsilylamine react similarly with alcohols, and here again the size and number of the radicals on the nitrogen affect the reaction. N,N,1,1,1-Pentaethylsilylamine reacts with alcohols much less readily than 1,1,1-triethylsilylamine, its N-methyl derivatives, and N,1,1,1-Tetraethylsilylamine.

EXPERIMENTAL

Preparation of 1,1,1-Triethyl-N-methylsilylamine. The apparatus in which the synthesis was carried out was a four-necked flask thermally insulated with asbestos and fitted with mercury-sealed stirrer, reflux condenser cooled with a mixture of dry ice and acetone, and thermometer. Over a period of ten minutes a solution of 44.5 g (0.30 mole) of chlorotriethylsilane in an equal volume of ether was added from a dropping funnel to 21 g (0.68 mole) of liquid methylamine. The precipitate of methylamine hydrochloride formed in the reaction was filtered off through a Buchner. Fractionation of the filtrate through a column gave 22.9 g (53.4 %) of 1,1,1-triethyl-N-methylsilylamine (for physical properties see Table 1).

Found %: C 57.8; H 12.59; Si 19.72; N 9.64. $C_7H_{19}SiN$. Calculated %: C 57.9; H 13.10; Si 19.30; N 9.65.

Preparation of 1,1,1-Triethyl-N,N-dimethylsilylamine. This was carried out similarly from 68 g (1.51 moles) of liquid dimethylamine and 57 g (0.37) mole of chlorotriethylsilane. The yield of 1,1,1-triethyl-N,N-dimethylsilylamine was 31.9 g (53.0 %).

Found %: C 60.5; H 13.00; Si 16.72; N 8.6. $C_8H_{21}SiN$. Calculated %: C 60.4; H 13.21; Si 17.54; N 8.8.

N,1,1,1-Tetraethylsilylamine. This was prepared similarly from 35 g (0.78 mole) of liquid ethylamine and 50 g (0.33 mole) of chlorotriethylsilane. The yield of N,1,1,1-tetraethylsilylamine was 32.9 g (62.3 %); found N 8.3 %; calculated N 8.8 %.

N,N,1,1,1-Pentaethylsilylamine. From 40.5 g (0.55 mole) of diethylamine and 34 g (0.23 mole) of chlorotriethylsilane we obtained 32.9 g (78 %) of N,N,1,1,1-pentaethylsilylamine; found N 7.2 %; calculated N 7.43 %.

1,1,1-Triethylsilylamine. From 170 g (10 moles) of liquid ammonia and 157.5 g (1.046 moles) of chlorotriethylsilane we obtained 90.7 g (66.2 %) of 1,1,1-triethylsilylamine. Found: molecular weight 134, N 10.3 %; calculated: molecular weight 131, N 10.7 %.

Determination of the Thermal Stabilities of 1,1,1-Triethylsilylamine and N,N,1,1,1-Pentaethylsilylamine. 1,1,1-Triethylsilylamine (9.88 g, i.e. 0.08 mole) was placed in a 100-ml round-bottomed flask fitted with reflux condenser protected by a calcium chloride tube and with a thermometer that reached to the bottom of the flask. In order to avoid the effects of moisture and atmospheric oxygen, before the experiment the flask was evacuated and filled with dry nitrogen. The triethylsilylamine was heated at the boil (142-144°) for seven hours and was then fractionated through a column. The weight of the fraction of boiling point 135-136° was 9.1 g (92 % recovery of the triethylsilylamine).

In a similar experiment 32.4 g (0.25 mole) of 1,1,1-triethylsilylamine was kept at the boil for 53 hours. Fractionation gave 28.5 g (88 %) of 1,1,1-triethylsilylamine and 2.7 g of a fraction of b.p. 235-246° (yield of hexaethyldisilazane 8.9 %). Found n_D^{20} 1.4485; d_4^{20} 0.8410; N 5.2 %; MR 78.24. Calculated: N 5.7 %; MR 79.01.

In a similar experiment 9.3 g (0.05 mole) of N,N,1,1,1-pentaethylsilylamine was heated at the boil for 25 hours. Fractionation gave 7.7 g (83 %) of N,N,1,1,1-pentaethylsilylamine and 1.3 g of a fraction of b.p. 200-216° and nitrogen content 0.9 %.

Reaction of 1,1,1-Triethylsilylamine with Chlorotriethylsilane. Mixtures of 1,1,1-triethylsilylamine and chlorotriethylsilane were kept in the cold or at the boil in the above-described apparatus (100-ml flask), after which the mixtures were fractionated from a flask fitted with a column. The results are given in Table 3.

TABLE 3

Reaction of 1,1,1-Triethylsilylamine with Chlorotriethylsilane

No.	Amounts taken		Reaction cond.		Hexaethyldisilazane formed				
	Triethylsilylamine	Chlorotriethylsilane	Temp. °C	Time (hours)	Yield (g)	Yield (%)	B.p. (°C)	Nitrogen content (%)	n_D^{20}
1	7.12	2.55	20	9[20]	0.87	10	Above 200	5.2	1.4460
2	6.75	2.42	160—170	9[20]	2.19	26	200—245	5.3	1.4460
3	7.80	2.90	20	94	2.18	31	242—245	5.3	1.4470
4	9.99	3.75	160—170	16	8.7	79	242—245	5.4	1.4475
5	9.93	11.33	160—170	16	10.0	81	244—245	5.4	1.4475

Hydrolysis of Silylamines

Hydrolysis of 1,1,1-Triethylsilylamine. A solution of 20 g (0.15 mole) of 1,1,1-triethylsilylamine in 25 ml of ether was placed in a three-necked flask fitted with stirrer, reflux condenser, and thermometer. Distilled water (4.14 g, i.e. 0.23 mole) was added, and during the first five minutes of stirring the temperature in the flask rose from 21.5° to 27°. The mixture was stirred vigorously for one hour, after which it was fractionated through a column.

The yield of the fraction of b.p. 152-154° (740 mm) (triethylsilanol) was 16.4 g (81.4 %); found: n_D^{20} 1.4335; d_4^{20} 0.8631; MR 39.79; OH 12.0 %; calculated: MR 39.89; OH 12.88 %.

Hydrolysis of 1,1,1-Triethyl-N-methylsilylamine. Analogous reaction between 5.1 g (0.035 mole) of 1,1,1--triethyl-N-methylsilylamine and 1.2 g (0.067 mole) of distilled water in 10 ml of ether was accompanied by a rise of temperature of 3°. Fractionation of the product gave 3.3 g (71 %) of triethylsilanol, b.p. 152-155° and n_D^{20} 1.4335.

Hydrolysis of 1,1,1-Triethyl-N,N-dimethylsilylamine. In reaction betweeen 6 g (0.038 mole) of 1,1,1-triethyl-N,N-dimethylsilylamine and 1.3 g (0.072 mole) of water the rise of temperature was 2°. Fractionation gave 4.2 g (84 %) of triethylsilanol, b.p. 152-154° and n_D^{20} 1.4335.

Hydrolysis of N,1,1,1-Tetraethylsilylamine. In reaction between 5.5 g (0.035 mole) of N,1,1,1-tetraethylsilylamine and 1.2 g (0.067 mole) of water the rise of temperature was 2°. Fractionation gave 3.2 g (70 %) of triethylsilanol,b.p. 148-152° (746 mm) and n_D^{20} 1.4335.

Hydrolysis of N,N,1,1,1-Pentaethylsilylamine. A mixture of 10 g (0.053 mole) of N,N,1,1,1-pentaethylsilylamine, 1.5 g (0.08 mole) of water, and 18 ml of ether was stirred for one hour and no change of temperature was observed. In the fractionation we recovered 9 g (90 %) of fraction of b.p. 65-69° (N,N,1,1,1-pentaethylsilylamine: n_D^{20} 1.4400; N 6.67 %).

In order to hydrolyze the compound in a homogeneous medium, a mixture of 8.2 g (0.04 mole) of N,N,1,1,1--pentaethylsilylamine, 1.5 ml (0.08 mole) of water, and 20 ml of acetone was stirred for one hour; in the early stages of stirring the temperature of the reaction mixture was observed to rise by 3°. Fractionation gave 4.23 g (73 %) of triethylsilanol, b.p. 58° (9 mm) and n_D^{20} 1.4335.

Replacement of the Amino Group by Alkoxyl: Reactions of 1,1,1-Triethylsilylamine

a) With Ethyl Alcohol. The apparatus consisted of a 40-ml still fitted with a film fractionation column designed for the separation of small amounts of material [7]. A mixture of 4 g (0.03 mole) of 1,1,1-triethylsilylamine and 2.8 g (0.06 mole) of absolute ethyl alcohol was prepared in the still. Shortly after mixing a vigorous reaction set in with liberation of ammonia and rise in the temperature of the mixture from 25° to 46°. After 3-4 hours at room temperature ammonia ceased to be liberated and the mixture was fractionated. The product, amounting to 3.92 g (80%), was ethoxytriethylsilane (for physical properties see Table 2).

Found %: C 59.8; H 12.59; Si 17.50. $C_8H_{20}OSi$. Calculated %: C 60.0; H 12.50; Si 17.50.

b) With Propyl Alcohol. The procedure was similar. In reaction between 4 g (0.03 mole) of 1,1,1-triethylsilylamine and 3.66 g (0.06 mole)of the alcohol the temperature rose from 25° to 42°. Fractionation gave 4.35 g (81 %) of triethylpropoxysilane.

Found %: C 61.6; H 12.76; Si 15.76; $C_9H_{22}OSi$. Calculated %: C 62.1; H 12.64; Si 16.09.

c) With Isopropyl Alcohol. In the analogous reaction of 4 g (0.03 mole) of 1,1,1-triethylsilylamine with 3.66 g (0.06 mole) of isopropyl alcohol the rise of temperature was 15°. Fractionation gave 4.4 g (77 %) of triethylisopropoxysilane.

Found %: C 61.3; H 12.85; Si 16.52. $C_9H_{22}OSi$. Calculated %: C 62.1; H 12.64; Si 16.09.

d) With Butyl Alcohol. In the analogous reaction of 4 g (0.03 mole) of 1,1,1-triethylsilylamine with 4.53 g (0.06 mole) of butyl alcohol the rise of temperature was 16°. Fractionation gave 4.58 g (80 %) of butoxytriethylsilane.

Found %: C 63.6; H 12.90; Si 14.80. $C_{10}H_{24}OSi$. Calculated %: C 63.8; H 12.76; Si 14.89.

e) With Isobutyl Alcohol. In the analogous reaction of 4 g (0.03 mole) of 1,1,1-triethylsilylamine with 4.53 g (0.06 mole) of isobutyl alcohol the rise of temperature was 14°. Fractionation gave 5.02 g (87 %) of triethylisobutoxysilane.

Found %: C 63.5; H 12.92; Si 14.93. $C_{10}H_{24}OSi$. Calculated %: C 63.8; H 12.76; Si 14.89.

f) With Isopentyl Alcohol. In the reaction of 4 g (0.03 mole) of 1,1,1-triethylsilylamine with 5.4 g of isopentyl alcohol the rise of temperature was 13°. Fractionation gave 4.76 g (77 %) of triethylisopentyloxysilane.

Found %: C 64.90; H 13.29; Si 13.92. $C_{11}H_{26}OSi$. Calculated %: C 65.3; H 12.87; Si 13.86.

g) With Octyl Alcohol. In the reaction of 2.9 g (0.022 mole) of 1,1,1-triethylsilylamine with 3.55 g (0.027 mole) of octyl alcohol the rise of temperature was 8°. Fractionation gave 3.31 g (61 %) of triethyloctyloxysilane.

Found %: C 69.2; H 13.24; Si 11.72. $C_{14}H_{32}OSi$. Calculated %: C 68.8; H 13.12; Si 11.39.

Reactions of 1,1,1-Triethyl-N-methylsilylamine

a) With Ethyl Alcohol. In the analogous reaction of 4 g (0.028 mole) of 1,1,1-triethyl-N-methylsilylamine with 1.5 g (0.054 mole) of absolute ethyl alcohol the rise of temperature was 18°. Ethoxytriethylsilane was isolated in the fractionation as a fraction of b.p. 152-154° (762 mm) and n_D^{20} 1.4160; yield 3.7 g (84 %).

b) With Isopentyl Alcohol. In the reaction of 3 g (0.021 mole) of 1,1,1-triethyl-N-methylsilylamine with 3.5 g (0.04 mole) of isopentyl alcohol the rise of temperature was 11°. Triethylisopentyloxysilane was isolated in the fractionation as a fraction of b.p. 201-203° (764 mm) and n_D^{20} 1.4240; yield 3.4 g (81 %).

Reactions of 1,1,1-Triethyl-N,N-dimethylsilylamine

a) With Ethyl Alcohol. In the reaction of 5 g (0.031 mole) of 1,1,1-triethyl-N,N-dimethylsilylamine with 2.9 g (0.063 mole) of absolute ethyl alcohol the rise of temperature was 13°. Ethoxytriethylsilane was obtained as fraction of b.p. 150-153° (754 mm) and n_D^{20} 1.4165; yield 3.94 g (78 %).

b) With Isopentyl Alcohol. In the reaction of 5 g (0.031 mole) of 1,1,1-triethyl-N,N-dimethylsilylamine with 5.6 g (0.063 mole) of isopentyl alcohol the rise of temperature was 9°. Triethylisopentyloxysilane was isolated in the fractionation as a fraction of b.p. 200-201° (748 mm) and n_D^{20} 1.4240; yield 4.6 g (72 %).

Reactions of N,1,1,1-Tetraethylsilylamine

a) With Ethyl Alcohol. In the reaction of 5 g (0.031 mole) of N,1,1,1-tetraethylsilylamine with 2.9 g (0.063 mole) of absolute ethyl alcohol the rise of temperature was 14°. Ethoxytriethylsilane was isolated in the fractionation as a fraction of b.p. 151.5-152.5° (745 mm) and n_D^{20} 1.4160; yield 3.6 g (72 %).

b) With Isopentyl Alcohol. In the reaction of 5 g (0.031 mole) of N,1,1,1-tetraethylsilylamine with 5.5 g (0.062 mole) of isopentyl alcohol the rise of temperature was 11°. Triethylisopentyloxysilane was isolated as a fraction of b.p. 198-203° (746 mm) and n_D^{20} 1.4240; yield 4.8 g (76 %).

Reactions of N,N,1,1,1-Pentaethylsilylamine

a) With Ethyl Alcohol. In the reaction of 2.61 g (0.014 mole) of N,N,1,1,1-pentaethylsilylamine with 1.3 g (0.03 mole) of absolute ethyl alcohol the rise of temperature was 5°. Ethoxytriethylsilane was isolated in the fractionation as a fraction of b.p. 150-154° (752 mm) and n_D^{20} 1.4160; yield 1.6 g (72 %).

b) With Isopentyl Alcohol. In the reaction of 2.1 g (0.011 mole) of N,N,1,1,1-pentaethylsilylamine with 1.9 g (0.022 mole) of isopentyl alcohol no rise in the temperature of the reaction mixture was noted. Triethylisopentyloxysilane was isolated as a fraction of b.p. 200-204° (750 mm) and n_D^{20} 1.4240; yield 1.55 g (69 %).

SUMMARY

1. In a study of the reactions of 1,1,1-triethylsilylamine and its N-alkyl derivatives (including the new compounds 1,1,1-triethyl-N-methylsilylamine and 1,1,1-triethyl-N,N-dimethylsilylamine) it was shown that treatment of these compounds with water causes the amino group to be replaced by hydroxyl and treatment with alcohols brings about replacement by alkoxyl.

2. The reaction of silylamines with aliphatic alcohols was applied in the synthesis of new compounds, namely alkoxytriethylsilanes $(C_2H_5)_3SiOR$ (R = propyl, isopropyl, butyl, isobutyl, isopentyl, and octyl).

3. It was shown that silylamines are of fairly good thermal stability and are not decomposed by long boiling.

LITERATURE CITED

[1] D. L. Bailey, L. H. Sommer and F. C. Whitmore, J. Am. Chem. Soc. 70, 435 (1948).

[2] R. Sauer and R. Hasek, J. Am. Chem. Soc. 68, 241 (1946).

[3] R. Sauer, J. Am. Chem. Soc. 66, 1707 (1944).

[4] B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, J. Gen. Chem. 24, 678 (1954).*

[5] Ch. Kraus and W. Nelson, J. Am. Chem. Soc. 56, 195 (1934).

[6] US Patent 2429883; C. A. 42, 922 (1948).

[7] A. Rose, Ind. Eng. Chem. 28, 210 (1936).

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PREPARATION AND PROPERTIES OF SOME ALKYLDEUTERIOSILANES

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Amoung the numerous and varied organosilicon compounds that have now been preparedthere are only a few containing not only hydrogen, but also its isotopes deuterium and tritium; these include CH_3SiD_3 [1, 2], $(C_6H_5)_3SiD$ [3], $(C_3H_7)_3SiT$ [4], and $(C_6H_5)_3SiT$ [4]. Somewhat more detailed study has been given to deuteriosilanes of the types SiD_4 [5-8], Si_2D_6 [5-7], Si_3D_8 [5-7], Si_4D_{10} [5-7], $SiDCl_3$ [9, 10], $SiDBr_3$ [9, 10], SiD_3F [11, 12], SiD_3Cl [12, 13], mainly from the point of view of their optical properties (radio-wave [1, 2, 8, 11, 13] and infrared [9, 12] spectra and Raman spectra [10]) and some other physical (boiling and melting points [5-7]) and chemical (thermal decomposition [7], reaction with DCl [8]) properties, with comparison of these with the properties of the corresponding protiosilanes. We also have been interested in comparing the properties of alkylsilanes containing silicon-attached hydrogen with those of the structural analogs containing silicon-attached deuterium, particularly with respect to their Raman spectra. We were interested also in the possibility of the use of lithium deuteride (LiD) for the synthesis of alkyldeuteriosilanes, for it has not been used previously for this purpose.

The use of LiD instead of LiH for the reduction of alkylchlorosilanes does not require any modification of procedure [14]. In this way we reduced the following alkylchlorosilanes: Cl_3SiCH_2Cl, $n\text{-}C_6H_{13}SiCl_3$, $Cl_3SiCH_2CH_2SiCl_3$, $(C_2H_5)_2SiCl_2$ and $(C_2H_5)_3SiCl$. The properties of the resulting alkyldeuteriosilanes, in comparison with those of the corresponding alkylprotiosilanes, are given in Table 1.

TABLE 1

No.	Formula of compound	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	Refraction of Si-D bond	Literature cited
1	D_3SiCH_2Cl	30.5 —	0.9630	1.4160	21.78	—	3.12	
	H_3SiCH_2Cl	30.5(739)	0.9286	1.4157	21.76	22.01	—	[15]
2	$n\text{-}C_6H_{13}SiD_3$	114 —	0.7389	1.4123	40.19	—	3.16	
	$n\text{-}C_6H_{13}SiH_3$	114 (751)	0.7182	1.4129	40.35	40.32	—	[15]
3	$D_3SiCH_2CH_2SiD_3$	47 —	0.7424	1.4107	32.17	—	3.19	
	$H_3SiCH_2CH_2SiH_3$	46 (746)	0.6987	1.4140	32.27	32.21	—	[14.16]
4	$(C_2H_5)_2SiD_2$	55 —	0.7005	1.3916	30.64	—	3.36*	
	$(C_2H_5)_2SiH_2$	55.3 (741)	0.6849	1.3915	30.63	30.83	—	[15]
5	$(C_2H_5)_3SiD$	107 —	0.7372	1.4117	39.57	—	3.31*	
	$(C_2H_5)_3SiH$	107 —	0.7302	1.4117	39.55	39.80	—	[17]

* If the refraction of the $Si-C_2H_5$ bond is taken as 2.38 [15].

It will be seen from Table 1 that replacement of silicon-attached hydrogen by deuterium has almost no effect on boiling point. The refractive index is also almost unchanged, but the density is raised substantially.*

* Similar changes in boiling point, refractive index, and density are observed also for deuteriohydrocarbons, such as deuteriobenzene [18]:

	B. p. (°C)	n_D^{20}	d_4^{20}
C_6H_6	80.07	1.5010	0.8787
C_6D_6	79.3	1.4997	0.9465

The data in Table 1 enable us to assume an average value of 3.23 ml/ mole for the refraction of the Si−D bond, i.e. almost the same as that of the Si−H bond, which, according to Warrick [19], is 3.20 ml/ mole and, according to Sauer [20], is 3.218 ml/ mole.

We now give the Raman spectra of four deuteriosilanes:

$(C_2H_5)_3SiD$ (I), $\Delta\nu$, cm^{-1}: 300 (0), 540 (4), 587 (6), 606 (1), 703 (0), 750 (1), 974 (4), 1020 (4b), 1047 (0b), 1110 (3), 1138 (0), 1235 (5), 1420 (3), 1470 (4), 1530 (6), 2105 (2), 2875 (10 sh), 2896 (10 sh), 2910(10sh), 2938 (3), 2960 (5).

$(C_2H_5)_2SiD_2$ (II), $\Delta\nu$, cm^{-1}: 238 (1), 310 (2), 406 (1 b), 504 (3), 520 (4), 568 (4), 615 (5), 640 (5), 683 (3), 707 (4), 960 (1), 975 (4), 1017 (4), 1112 (2), 1235 (5), 1416 (3), 1467 (4), 1542 (10), 1553 (3), 2130 (2), 2875 (9 sh), 2895 (10 sh), 2910 (3 sh), 2936 (4), 2960 (5).

$C_6H_{13}SiD_3$ (III), $\Delta\nu$, cm^{-1}: 202 (2), 280 (0), 366 (0), 420 (1), 600 (0), 645 (4), 668 (3 sh), 685 (4), 730 (1), 748 (3 b), 800 (1), 845 (1 b), 952 (1 b), 1070 (0 b), 1110 (4), 1184 (5), 1240 (0), 1307 (5 b), 1410 (1), 1442 (4), 1450 (4), 1549 (10), 1571 (5), 2156 (2), 2857 (7), 2895 (10), 2920 (2), 2938 (6), 2965 (5).

$D_3SiCH_2CH_2SiD_3$ (IV), $\Delta\nu$, cm^{-1}: 170 (2), 452 (5), 591 (1), 639 (2), 684 (5), 705 (1), 762 (4), 1020 (1 b), 1113 (1 b), 1252 (6), 1417 (2), 1552 (10), 1575 (4), 2155 (2), 2895 (7), 2910 (2).

Comparison of the spectra reveals intense lines in the region 1550-1580 cm^{-1} attributable [12, 21] to valence vibrations of Si−D. There are two Si−D frequencies in (II) − (IV), of which the first, the lower frequency, is much more intense than the second. This shows that, in contrast with the case of Si−H bonds in compounds of the type $R_{4-n}SiH_n$ (n = 2 or 3 and R is an aliphatic radical), interaction exists between Si−D bonds and results in the appearance of symmetrical (intense line) and antisymmetrical (degenerate) frequencies in (II) − (IV). The value of $\frac{\nu_c + \nu_{ac}}{2}$ varies in accordance with the same law as that established for the frequencies of the valence vibrations of Si−H [22] and falls with reduction of the number of D atoms attached to Si: about 1560 for (III) and (IV), 1548 for (II), and 1530 for (I). By using the usual relationships for isotopic frequencies $\frac{\nu_1^2}{\nu_2^2} = \frac{M_2}{M_1}$, in which ν and ν_2 are the Si−H and Si−D frequencies respectively and M_1 and M_2 are the reduced masses of these systems, we may obtain ν from ν_2, and values obtained being 2150, 2135, and 2105 cm^{-1} (in the order − SiH_3, = SiH_2, ≡ ≡SiH). These values correspond to frequencies found for the structurally analogous protiosilanes [16] and in our spectra of (I) − (IV). In explanation of this last fact we may suppose the presence of small amounts (not more than 5 %) of protiosilanes in our preparations.

In our paper [22] we drew attention to the constant value of the deformation frequency of H−Si−H at 945 cm^{-1}. In the investigation [12] an analogous frequency in compounds of the type $FSiD_3$ and $ClSiD_3$ was observed at about 700 cm^{-1}. On this basis we may assume that the stable and comparatively intense line at 684 cm^{-1} in (II) − (IV) is to be attributed to the D−Si−D deformation vibration in these compounds. In accord with this assumption, the frequency 685 cm^{-1} is not observed in (I). The lowering noted above in the frequencies ν(Si−D) with reduction in the number of Si-attached D atoms is not general for all compounds containing an Si−D bond, but is probably peculiar to compounds of the type D_nSiR_{4-n} (R is aliphatic). According to [12, 23] for compounds of the type D_nSiCl_{4-n} the opposite effect may be observed: rise in the Si−D frequency with reduction in the number of D atoms and increase in the number of chlorine atoms; thus in D_3SiCl the Si−D frequencies are 1584 and 1619 cm^{-1} (average 1600 cm^{-1}) and in $DSiCl_3$ the frequency is 1647 cm^{-1}. On the basis of this it may be considered that the way in which the frequency changes is associated with the character of the electron shell of the the third atom (Cl, C, etc.), the effect of which on the mobile electron shell of the Si atom results in its displacement in the direction of Si−D bonds or in the opposite direction.

We must point out also the features found in common in the spectra of the deuterio- and analogous protio--silanes. There are data in the literature on the spectra of the analogs of (III) and (IV); the Raman spectrum of the analog of (II), $H_2Si(C_2H_5)_2$, is given below.* Comparison of the spectra of (II) and $(C_2H_5)_2SiH_2$ reveals the common frequencies 975, 1017, 1233, 1415, ~1465, 2875, 2895, 2915, 2935, 2960 cm^{-1}, i.e. frequencies belonging to deformation and valence vibrations in a C_2H_5 group attached to Si [24]. Similarly, in the spectra of (III) and

* $H_2Si(C_2H_5)_2$, $\Delta\nu$, cm^{-1}: 145 (4), 172 (0), 295 (2), 318 (1), 360 (4 b), 606 (10), 640 (2), 670 (2), 710 (3), 767 (3 b), 843 (0), 941 (4), 970 (4), 1017 (4), 1233 (5), 1298 (1), 1314 (1), 1415 (4), 1460 (4), 2130 (10 b), 2875 (10), 2895 (10), 2915 (6), 2935 (5), 2958 (10), $H_2Si(C_2H_5)_2$. This spectrum was determined by B. A. Sokolov.

TABLE 2

No.	Formula of original compound	B.p.(°C)	Amount (g)	Amount of LiD (g)	Solvent (ml)	Reduction product	Amount (g)	Yield (%)	Found %				Calculated %			
									C	H+D	Si	Cl	C	H+D	Si	Cl
1	$ClCH_2SiCl_3$	118	60	8	Dioxane 60	$ClCH_2SiD_3$	7.6	28	14.68	9.79	—	41.68	14.37	9.64	—	42.42
									14.47	9.85	—	41.10				
2	$n\text{-}C_6H_{13}SiCl_3$	187—190	33	9.5	Dibutyl ether 50	$n\text{-}C_6H_{13}SiD_3$	9.6	54	60.58	15.79	23.04	—	60.42	16.05	23.33	—
									60.64	15.88	23.38					
3	$Cl_3SiCH_2CH_2SiCl_3$	200	30	10	Dioxane 60	$D_3SiCH_2CH_2SiD_3$*	7.5	55	—	—	—	—	—	—	—	—
4	$(C_2H_5)_2SiCl_2$	129	40	9	Dioxane 60	$(C_2H_5)_2SiD_2$	17.5	76	52.94	15.34	30.83	—	53.25	15.64	31.11	—
									53.10	15.35	30.72					
5	$(C_2H_5)_3SiCl$	147	31	4	Dibutyl ether 50	$(C_2H_5)_3SiD$	7.4	31	61.68	14.44	22.84	—	61.46	14.61	23.93	—
									61.75	14.40	21.52					

* For $D_3SiCH_2CH_2SiD_3$, as also for $H_3SiCH_2CH_2SiH_3$ [14], we did not succeed in obtaining satisfactory results for elementary analysis under the usual conditions.

$H_3SiC_6H_{13}$ [4] we find the common lines: 750, 795, 1070, ~1100, 1184, 1240, 1306, 1410, 1450, 2857, 2895, 2920, 2938, 2965 cm^{-1}, probably characterizing vibrations in the hexyl chain. The same phenomenon is observed in (IV) and $H_3SiCH_2CH_2SiH_3$: 1113, 1251, 1417, 2892, 2910 cm^{-1}. In contrast to this, the region of the spectrum below 700 cm^{-1}, which includes the valence and deformation vibrations of silicon-carbon systems (C – Si – C, Si – C) and deformation vibrations of e.g. D – Si – D, is, as already indicated, greatly different for the deuterio- and protio-silanes with respect to the positions of frequencies.

This difference in the spectra of the deuterio- and protio-silanes is to be explained by changes in the form of vibrations and therefore in the frequencies of the silicon-carbon skeleton due to replacement of H by D. This replacement has little effect on remote internal vibrations of carbon chains and CH_2 and CH_3 groups.

EXPERIMENTAL

The reduction of alkylchlorosilanes to the corresponding deuterium compounds was carried out, under the conditions described previously for the preparation of alkylsilanes containing silicon-attached hydrogen, in a still having a small rectifying column [14]. Data on the experimental conditions and the analysis of the products are given in Table 2. The alkyldeuteriosilanes obtained were refractionated through a column over a little LiD. The properties of compounds distilled in this way are given in Table 1.

SUMMARY

1. It was shown that alkyldeuteriosilanes can be prepared from the corresponding alkylchlorosilanes by reducing them with LiD.

2. Fine new alkyldeuteriosilanes were prepared, and some of their physical properties were studied. It was shown that the frequencies of the valence vibrations of Si–D fall in the region 1530-1570 cm^{-1} and are lowered by reduction of the number of D atoms attached to Si. It was found that the refraction of the Si – D bond is 3.23 ml/ mole.

LITERATURE CITED

[1] D. R. Lide and D. K. Coles, Phys. Rev. 80, 911 (1950); C. A. 45, 1424 (1951).

[2] B. P. Dailey, Ann. N. Y. Acad. Sci. 55, 915 (1952); C. A. 47, 2563 (1953).

[3] H. Gilman, G. E. Dunn and G. S. Hammond, J. Am. Chem. Soc. 73, 4499 (1951).

[4] L. Kaplan, and K. E. Wilzbach, J. Am. Chem. Soc. 74, 6152 (1952).

[5] K. Stockland, Kgl. Norske Videnskad. Selskabs Forh. 12, 122 (1939); C. A. 35, 2380 (1941).

[6] K. Stockland, Kgl. Norske Videnskad Selskabs. Forh. 19, No. 10, 33 (1946); C. A. 41, 7182 (1947).

[7] K. Stockland, Kgl. Norske Videnskad Selskabs, Skrifter, No. 3, 1 (1950); C. A. 46, 5412 (1952).

[8] B. Bak, J. Bruhn, and J. Rastrup-Andersen, Acta Chem. Scand. 8, 367 (1954); C. A. 48, 10437 (1954).

[9] F. Halverson, Rev. Modern Phys. 19, 87 (1947); C. A. 42, 36 (1948).

[10] J. M. Delfosse, Nature 137, 868 (1936); C. A. 30, 5498 (1936).

[11] B. Bak, J. Bruhn and L. Rastrup-Andersen, J. Chem. Phys. 21, 752 (1953); C. A. 47, 6770 f (1953).

[12] F. A. Andersen, and B. Bak, Acata Chem. Scand. 8, 738 (1954); C. A. 48, 13427 (1954).

[13] B. Bak, J. Bruhn, and L. Rastrup-Andersen, J. Chem. Phys. 21, 753 (1953); C. A. 47, 7324 (1953).

[14] A. D. Petrov and V. A. Ponomarenko, Proc. Acad. Sci. USSR 90, No. 3, 387 (1953); A. D. Petrov, V. A. Ponomarenko, and V. I. Boikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 504.*

[15] V. A. Ponomarenko and V. F. Mironov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 497.*

[16] M. I. Batuev, V. A. Ponomarenko, A. D. Matveeva, and A. D. Petrov, Proc. Acad. Sci. USSR 95, 805 (1954).

---

* Original Russian pagination. See C. B. Translation.

[17] F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, J. Am. Chem. Soc. 69, 2108 (1947).

[18] G. Egloff, Physical Constants of Hydrocarbons 25, 37 (1946).

[19] E. L. Warrick, J. Am. Chem. Soc. 68, 2455 (1946).

[20] R. O. Sauer, J. Am. Chem. Soc. 68, 954 (1946).

[21] N. Kaplan, J. Am. Chem. Soc. 76, 5880 (1954).

[22] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and Iu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 310.*

[23] J. M. Delfosse, Nature 137, 868 (1936).

[24] H. Murata, R. Okawara, and T. Watase, J. Chem. Phys. 18, 1308 (1950).

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PROPERTIES OF SOME VINYL ESTERS

COMMUNICATION 1. POLYMERIZATION AND RATE OF HYDROLYSIS OF MONOMERS

E. N. Rostovskii, S. N. Ushakov and A. N. Barinova

Several investigations have been published recently on the properties of homologs of vinyl acetate, namely, vinyl formate [1, 2], vinyl laurate, vinyl palmitate, vinyl stearate [3, 4], and also esters of aromatic [5, 6] and fluorine-substituted [7] acids. Apart from these cases, information on the properties of vinyl esters is generally confined to data on the boiling points and some other physical constants of the monomers. There are only isolated papers [1, 3, 4] in which the properties of polyvinyl esters have been studied in detail. More detailed comparison of properties in homologous series is desirable, for the presence of various substituents in the molecule can substantially change the overall result of the polymerization of a given monomeric ester, the kinetics of the process, the character of chain termination, and the appearance of branching. It is of importance also to compare the effects of various functional groups in the vinyl compound on the properties of the monomer and the corresponding polymer.

The present communication concerns an investigation into the kinetics of the polymerization of some vinyl esters, determination of their rates of hydrolysis, and measurement of the glass temperatures of the polymers. Subsequent communications will be concerned with other properties and with matters relating to processes occurring during polymerization.

No comparative studies of the kinetics of the polymerization of various vinyl esters have been carried out previously. The question of the mechanism of the acceleration of polymerization in its middle stages is also still unresolved. This acceleration is quite notable for methacrylic derivatives [8] and is generally absent for styrene and vinyl acetate. However, some investigators have observed the so-called gel effect for these monomers also [9, 10].

We studied also the kinetics of the hydrolysis of vinyl esters, considering it desirable, in later work, to compare the rates of hydrolysis of monomeric and polymeric esters. The positive or negative inductive effect of a substituent in the acyl group and its effect on the electrophilic character of the carbonyl oxygen will undoubtedly affect the stability of the ester linkage. The hydrolysis of various esters has been studied [11-14]. By the method of isotopic exchange it was shown [11, 14] that in the hydrolysis of carboxylic esters it is mainly the bond between the carbonyl carbon and the oxygen of the alcohol residue that is broken. Kravchenko and Penzova [12] established the following relative rates of hydrolysis: ethyl acetate 7.1, ethyl isobutyrate 1, ethyl benzoate 0.4. A similar relation was found by Reicher [13], who noted also the small effect of the nature of the alcohol residue on the rate of hydrolysis, as compared with that of the acyl group. This behavior was confirmed in our investigations.

In order to determine the effect of the acyl radical on the properties of the polymer, the glass (vitrification) temperatures T_g of the polymers were determined. Comparison of polymers with the aid of this characteristic is facilitated by the fact that, beyond a certain limit, T_g is independent of the molecular weight of the polymer [15]. Study of the brittle points and glass temperatures of various polyacrylates and polymethacrylates of alcohols of normal and, sometimes, branched structure [16, 17] indicated the presence of minimum glass and brittle points for alkyl groups of a certain chain length and higher glass points for polymers having branched alkyls, as compared with their normal isomers.

EXPERIMENTAL

Vinyl formate, butyrate, isobutyrate, isovalerate, hexanoate, and benzoate were synthesized by methods

described by us in previous papers [2, 18]. We generally preferred vapor-phase heterocatalytic synthesis from acetylene and the acid, since it gives monomers that have the high purity essential for kinetic investigations of polymerization. Vinyl chloroacetate was prepared in the liquid phase by reaction between acetylene and the acid at 70-80° in presence of a mercury catalyst. The washed, dried, and rectified monomers were finally purified by further careful rectification through a laboratory column having a still head with controlled reflux ratio. In order to prevent the formation and subsequent decomposition of peroxy compounds, fractionation of the monomers, apart from vinyl formate and acetate, was carried out in a vacuum and in an atmosphere of purified nitrogen. Table 1 gives the physical constants of the monomers.

Polymerization of Vinyl Esters. Polymerization was carried out in the mass under nitrogen in presence of 0.053 mole % of benzoyl peroxide in sealed ampoules having two side tubes; a temperature of 80 ± 0.1° was maintained with an ultrathermostat. At suitable intervals ampoules were removed from the thermostat, rapidly cooled, and opened. The yield of polymer was determined by estimating the amount of residual monomer by bromination with methanolic bromine. In some cases, when polymerization was carried to a more advanced stage, parallel determinations of the amount of polymer formed were made, the polymer being precipitated, filtered off, and dried. The results of the polymerization experiments are given in Fig. 1. It will be seen from Fig. 1 that increase in the length of the acyl radical, and also increase in its ramification, reduces the rate of polymerization. This phenomenon can be explained a) by the effect of the acyl radical on the polarization of the double bond, and b) by steric hindrance associated with the structure of the radical. Vinyl formate polymerizes more rapidly than vinyl acetate. At 80° with a benzoyl peroxide content of 0.035 mole %, in 20 minutes the progress of the polymerization of vinyl formate attains about 50 % and that of vinyl acetate about 30 %. Unlike the chloro derivatives of styrene, which polymerize more rapidly than styrene itself [19], vinyl chloroacetate polymerizes less rapidly than vinyl acetate. This phenomenon must probably be associated with the higher reactivity of the acyl group and its more vigorous reaction with free radicals.

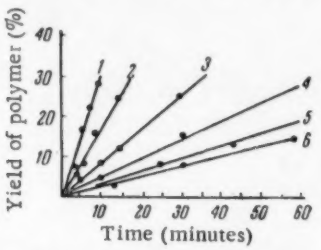

Fig. 1. Polymerization of vinyl esters: 1) vinyl acetate; 2) vinyl butyrate; 3) vinyl isobutyrate; 4) vinyl isovalerate; 5) vinyl chloroacetate; 6) vinyl hexanoate.

TABLE 1

No.	Monomer	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated
1	Vinyl formate	46 (760)	0.9585	1.3845	17.58	17.24
2	Vinyl butyrate	64.5 (130)	0.9299	1.4120	31.07	31.095
3	Vinyl isobutyrate	54 (125)	0.8915	1.4056	31.405	31.095
4	Vinyl isovalerate	50 (39)	0.8863	1.414	36.01	35.71
5	Vinyl hexanoate	36.5 (3)	0.8870	1.4220	40.68	40.33
6	Vinyl benzoate	82.5 (3)	1.0678	1.5260	42.64	42.35
7	Vinyl chloroacetate	37 (7)	1.1864	1.4456	27.06	26.72

Kinetics of the Hydrolysis of Vinyl Esters. Hydrolysis was carried out in alcoholic caustic alkali at 25 ± 0.2°. After the addition of an alcoholic solution of the ester the alkali concentration was 0.05 N; 95.5 % ethanol was used. In the case of rapidly hydrolyzable monomers, separate ester samples were introduced into the solution for each test; monomers that hydrolyzed slowly (as shown by preliminary tests) were dissolved in alcohol, and the required amount of this solution was mixed with the alkali solution. After definite intervals a slight excess of cooled 0.1 N acid was added to test samples to stop hydrolysis, and the excess was back-titrated. Apart from the monomers listed in Table 1, ethyl acetate and vinyl crotonate [b.p. 33° (17 mm); d_4^{20} 0.942] were examined. The second-order rate constants and relative rates of hydrolysis are given in Table 2.

By special experiments with vinyl chloroacetate and chloroacetic acid, it was shown that the error due to hydrolytic removal of chlorine on saponification with alkali does not exceed 2-3% at 25°.

From Table 2 and available data on ethyl esters [12, 13] we may draw certain conclusions. The dependence of rate of hydrolysis on the structure of the acyl group is about the same for vinyl esters as it is for ethyl esters. A double bond in the alcohol residue has little effect on the stability of the ester linkage. Vinyl isobutyrate is hydrolyzed more slowly than vinyl butyrate, which must be associated with the inductive (electron-donating) effect of the second methyl group. The presence of chlorine in the acyl radical greatly reduces the stability of the ester linkage. Comparison of crotonic and butyric esters shows that introduction of a double bond into the acyl radical reduces the rate of hydrolysis almost threefold. In this case the effect of conjugation may be of importance; the phenomenon should be examined over a wider range of examples. As shown by the experiments with vinyl acetate, presence of water in the reaction medium instead of ethanol accelerates hydrolysis by a factor of several hundred. In the case of other esters their solubility in water will affect the extent of the acceleration of hydrolysis.

TABLE 2

No.	Ester	Hydrolysis rate constant × 10^3	Relative rate of hydrolysis*
1	Vinyl chloroacetate	348.5	600
2	Vinyl formate	202.4	~350
3	Vinyl acetate	0.580	1
4	Ethyl acetate	0.592	~ 1
5	Vinyl butyrate	0.1281	0.22
6	Vinyl isobutyrate	0.0727	~ 0.124
7	Vinyl benzoate	0.0563	~ 0.1
8	Vinyl isovalerate	0.0492	0.085
9	Vinyl crotonate	0.046	0.079
10	Vinyl acetate**	214.8**	370**

*Rate of hydrolysis of vinyl acetate = 1.

**Hydrolysis with aqueous alkali.

Glass Temperatures of Polymers. Glass temperatures were determined* from deformation characteristics in a Marei Apparatus [20]. For the complete removal of monomers and sorbed substances the polymers were first heated to constant weight at 60° in thin layers in a vacuum. The T_g values obtained are given in Fig. 2. In this figure the broken line represents softening temperatures (from the literature [3]) for polyvinyl esters of acids having 12, 14, 16, and 18 carbon atoms, determined refractometrically by Port, Hansen, Jordan, Deitz, and Swern. Although these investigators attributed the temperatures that they obtained to phase transitions of the first kind, we considered it possible to compare these points with our results since in other cases, for example for polyvinyl acetate [21, 22], the refractometric method of determining glass points gave results very close to those that we obtained by Marei's method on the same polymer. Points 1 and 2 on Fig. 2 are T_g values determined by us for polyvinyl chloroacetate and benzoate.

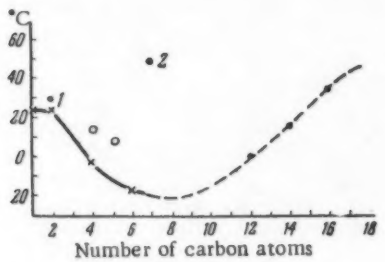

Fig. 2. Dependence of T_g on the number of carbon atoms in the acyl group (× — normal structure; o — branched structure). The broken line represents the results of Port et al. [3]. 1) T_g for polyvinyl chloroacetate; 2) T_g for polyvinyl benzoate.

It follows from Fig. 2 that the effect of side groups in polymer chains and of their branched structure in various vinyl esters is analogous to that established previously [16, 17] for polyacrylates and polymethacrylates. The rise in the glass temperature for polymers having long acyl groups may be explained, as in the case of acry-

* A. I. Volkova took part in this work.

lates and methacrylates [3, 23], by the appearance of a crystalline phase. Hence, the presence of a minimum T_g in a homologous series is evidently due to the superposition of two factors: 1) gradual lowering of the glass temperature of the amorphous phase with increase in the length of the acyl radical, and 2) the effect of the crystallites that are formed. This type of behavior should be general for polymers in various homologous series.

SUMMARY

1. A study was made of the mass polymerization and rate of hydrolysis of various vinyl esters; the glass temperatures of their polymers were determined.

2. The effect of the structure of the acyl group on the initial rate of polymerization and on the kinetics of the hydrolysis of these esters was determined.

3. It was shown that the effect of the size and structure of side groups of polymers on their glass temperatures is similar in character for vinyl esters, acrylic esters, and methacrylic esters.

LITERATURE CITED

[1] A. A. Vansheidt and L. F. Chelpanova, J. Gen. Chem. 20, 226 (1950).*

[2] S. N. Ushakov, I. A. Arbuzov, and E. N. Rostovskii, J. Appl. Chem. 20, 1013 (1947).

[3] W. Port, J. Hansen, E. Jordan, T. Deitz and D. Swern, J. pol. Sci. 7, 207 (1951).

[4] L. Craig, R. Kleinschmidt, E. Miller, J. Wilkinson, R. Davis and C. Montross and W. Port, Ind. Eng. Chem. 47, 1702 (1955).

[5] G. Ham and E. Ringwald, J. pol. Sci. 8, 91 (1952).

[6] G. Smets and A. Hertoghe, Makromol. Chem. 17, 189 (1956).

[7] F. Reid, D. Codding and T. Bovey, J. pol. Sci. 18, 417 (1955).

[8] G. Schulz and E. Harborth, Makromol. Chem. 1, 106 (1947).

[9] H. Melville, Nature 158, 553 (1946).

[10] A. N. Pravednikov, Questions of Chemical Kinetics, Catalysis, and Reactivity, Izd. AN SSSR, Moscow, 1955, p. 320.

[11] M. Polanj and Z. Szabo, Trans Faraday Soc. 30, 508 (1934).

[12] A. Kravchenko and V. Penzova, J. Gen. Chem. 20, 2076 (1950).*

[13] I. A. Kablukov, E. I. Gapon, and M. A. Grindel', Physical and Colloid Chemistry, Agriculture Press, Moscow, 1942, p. 156.

[14] A. I. Brodskii, Chemistry of Isotopes, Izd. AN SSSR, Moscow, 1952, p. 248.

[15] P. P. Kobeko, Amorphous Substances, Izd. AN SSSR, Moscow and Leningrad, 1952, p. 179.

[16] C. Rehberg and C. Fisher, Ind. Eng. Chem. 40, 1429 (1948).

[17] P. P. Kobeko and N. M. Kummatskaia, Collected Papers in Honor of the 70th Birthday of Academician A. F. Ioffe, Izd. AN SSSR, Moscow, 1950, p. 242.

[18] E. N. Rostovskii and A. N. Barinova, J. Appl. Chem. 27, 1101 (1954).*

[19] A. F. Dokukina, M. M. Koton, K. N. Kriukova, O. K. Mineeva, and V. A. Poribok, J. Gen. Chem. 30, 190 (1956).*

[20] A. I. Marei, Chemistry and Physical Chemistry of Macromolecular Compounds, Izd. AN SSSR, Moscow, 1952, p. 274.

[21] R. Wiley, J. pol. Sci. 2, 10 (1947).

[22] R. Wiley, G. Brauer, J. pol. Sci 3, 455 (1948).

[23] H. Kaufmann, A. Sacher, T. Alfrey, J. Fankuchen, J. Am. Chem. Soc. 70, 9147 (1948).

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INVESTIGATION OF THE FREE-RADICAL MECHANISM OF THE ADDITION OF POLYHALO COMPOUNDS TO VINYL ACETATE

M. F. Shostakovskii and L. I. Shmonina

The addition of polyhalo compounds of carbon and silicon to vinyl compounds in presence of peroxides, which proceeds by a free-radical mechanism, is of undoubted scientific and practical interest. The reactions that have been studied most fully are those of polyhalomethanes and trichlorosilane with various olefins and vinyl ethers [1-5]. There has been work also on the addition of silicon tetrachloride to olefins and to carbon monoxide [6].

Less study has been devoted to the reactions of these compounds with vinyl esters, in particular vinyl acetate. There is only an American patent (1946) [7], in which there is a brief indication of the conditions for reaction between carbon tetrachloride and vinyl acetate. The reaction gave some polymers of low molecular weight having the general formula $CCl_3(CH_2CHOCOCH_3)_nCl$, in which n varied from 1 to 8. The patent does not indicate the yield of the product, which is characterized only by boiling point.

The present paper is concerned with the relative activities of carbon tetrachloride, chloroform, silicon tetrachloride, trichlorosilane, and dichloroethylsilane in the addition reaction with vinyl acetate in presence of benzoyl peroxide, and also with the effect of reaction conditions (concentration, temperature, time of heating, and amount of benzoyl peroxide) on the yield of the products of equimolecular addition. In the case of carbon tetrachloride the yield of equimolecular-addition product increases considerably with increase in the amount of CCl_4 and attains 62 % under optimum conditions. Under these conditions no addition products having a degree of polymerization of $n > 1$ are formed. Reaction proceeds as follows:

$$CH_2 = CHOCOCH_3 + CCl_4 \rightarrow CCl_3CH_2\overset{\displaystyle Cl}{\underset{|}{C}}H - OCOCH_3.$$

Variation of temperature and time of heating has no appreciable effect.

In the reaction of vinyl acetate with chloroform no equimolecular-addition product ($CCl_3CH_2CH_2OCOCH_3$) is formed. A product was isolated which, on the basis of elementary analysis, could be assigned the structure $CCl_3(CH_2CHOCOCH_3)_9CH_2CH_2OCOCH_3$. However, molecular weight determination indicated that a mixture of low-molecular-weight polymers (n = 6-9) was probably formed.

It was of considerable interest to investigate also the addition of some chlorosilanes to vinyl acetate. It was found that silicon tetrachloride does not react with vinyl acetate. Under mild conditions (60-100°, 0.01 mole of benzoyl peroxide) the substances taken were recovered unchanged, but under more severe conditions (100°, heating in sealed tubes, 0.02-0.023 mole of benzoyl peroxide) the vinyl acetate polymerized and the silicon tetrachloride taken was recovered almost completely. In the case of trichlorosilane and dichloroethylsilane, under mild conditions addition again did not occur, but under more severe conditions equimolecular-addition products were isolated: $CH_2 = CHOCOCH_3 + SiHCl_3 \rightarrow SiCl_3CH_2CH_2OCOCH_3$.

We assigned these structures to the addition products on analogy with the structures of the products of the addition of CCl_4 to vinyl acetate and of $SiHCl_3$ to vinyl ethers [3-5] and also on the basis of the free-

-radical mechanism of the reactions, which can be represented as follows:

$$CCl_4 \xrightarrow{(C_6H_5CO)_2O_2} \dot{C}Cl_3 + Cl$$

$$CCl_3 + CH_2 = CHOCOCH_3 \rightarrow CCl_3CH_2\dot{C}HOCOCH_3$$

$$CCl_3CH_2\dot{C}HOCOCH_3 + CCl_4 \rightarrow CCl_3CH_2CHClOCOCH_3 + \dot{C}Cl_3$$

$$CCl_3CH_2\dot{C}HOCOCH_3 + nCH_2 = CHOCOCH_3 \rightarrow CCl_3(CH_2CHOCOCH_3)_n \atop {\quad\quad\quad\quad\quad\quad\quad\quad |\ CH_2\dot{C}HOCOCH_3}$$

$$CCl_3(CH_2CHOCOCH_3)_n + CCl_4 \rightarrow CCl_3(CH_2CHOCOCH_3)Cl + \dot{C}Cl_3 \ldots$$
$$|\ CH_2\dot{C}HOCOCH_3$$

EXPERIMENTAL

The reactants used in this work had the following constants: vinyl acetate, b.p. 72-73°; carbon tetrachloride, b.p. 75-76°; silicon tetrachloride, b.p. 56°; chloroform, b.p. 60-61°; trichlorosilane, b.p. 32-34°; dichloroethylsilane, b.p. 74°.

Addition of CCl_4 to Vinyl Acetate. A mixture of 5 g of vinyl acetate and 392 g of CCl_4 was refluxed in a round-bottomed flask for 10-15 minutes. Benzoyl peroxide (0.01 g) was then added to the hot solution, and boiling was continued for ten hours. Unchanged CCl_4 and vinyl acetate was distilled off, and vacuum distillation of the residue gave 8.7 g of 1,3,3,3-tetrachloropropyl acetate, b.p. 60° (1 mm); n_D^{20} 1.4730; d_4^{20} 1.445; found MR 46.59; calculated MR 46.41.

Found %: C 25.11; 25.18; H 2.54; 2.52; Cl 59.50; 59.55. $C_5H_6O_2Cl_4$. Calculated %: C 25.02; H 2.55; Cl 59.11.

The yield of 1,3,3,3-tetrachloropropyl acetate was 62 % on the amount of vinyl acetate taken. The literature [7] gives b.p. 62.5° (0.9 mm).

All the remaining experiments were carried out under the conditions described, and the following results were obtained (Table 1).

TABLE 1

Molar ratio of vinyl acetate to CCl_4	Yield of product (% on vinyl acetate taken)	Molar ratio of vinyl acetate to CCl_4	Yield of product (% on vinyl acetate taken)
1 : 1	0	1 : 10	30
1 : 2.5	8-10	1 : 20	40
1 : 5	23	1 : 40	62

Addition of $CHCl_3$ to Vinyl Acetate. A mixture of 20 g of vinyl acetate, 277 g of chloroform, and 0.05 g of benzoyl peroxide was heated as described for the reaction with CCl_4. Fractionation of the reaction mixture gave 260 g of unchanged chloroform and 25 g of light-yellow residue which did not distill over at 1 mm. The residue was precipitated from benzene with petroleum ether; the product was found to contain halogen. It was dried in a vacuum desiccator at 40-60° (appreciable darkening in color) and was then analyzed:

Found %: C 49.32; 49.40; H 6.34; 6.49; Cl 10.33; 10.57. $C_{41}H_{61}O_{20}Cl_3$. Calculated %: C 50.00; H 6.20; Cl 10.80

The analytical results correspond to the formula $CCl_3(CH_2CHOCOCH_3)_9CH_2CH_2OCOCH_3$, n = 9, found M 839; 833; calculated (for a mixture with n = 6, 7, 8 and 9) M 869.

Addition of $SiCl_4$ to Vinyl Acetate. A mixture of 10 g of vinyl acetate, 205 g of $SiCl_4$, and 0.02 g of benzoyl peroxide was heated as described for the reaction with CCl_4. In the fractionation the reaction mixture distilled without leaving a residue, and the distillate was found to be a mixture of the starting materials. All the

remaining experiments were carried out in sealed tubes, and the results are presented in Table 2.

TABLE 2

No.	Amount (g)			Time of heating (hours)	Temperature (°C)	Notes
	Vinyl acetate	$SiCl_4$	Benzoyl peroxide			
1	4.5	200	0.01	10	100	Reaction mixture distilled without residue
2	8.6	34	0.6	10	100	32.7 g of $SiCl_4$ recovered unchanged; 7.5 g of polymeric residue
3	8.6	34	0.6	5	60	34 g of $SiCl_4$ recovered unchanged; 7.8 g of polymeric residue
4	8.6	34	0.6	8 months	at room temperature	33 g of $SiCl_4$ recovered unchanged; 7.5 g of polymeric residue

Addition of $SiHCl_3$ to Vinyl Acetate. 1) A mixture of 13 g of vinyl acetate, 30.8 g of $SiHCl_3$, and 0.02 g of benzoyl peroxide was heated in a sealed tube in a boiling water bath for 40 hours. Fractionation gave 28.2 g of unchanged $SiHCl_3$, 7.2 g of unchanged vinyl acetate, and 4.5 g of a dark-colored residue which did not distill at 1 mm. 2) A mixture of 30 g of vinyl acetate, 53 g of $SiHCl_3$, and 1.8 g of benzoyl peroxide was heated as indicated above for 20 hours. Fractionation of the reaction mixture gave 41 g of $SiHCl_3$, 8.6 g of vinyl acetate, 5.5 g of intermediate fractions, 15 g of nondistillable residue, and 8 g of 2-(trichlorosilyl)ethyl acetate as a colorless mobile liquid, b.p. 64.5-66.5° (6 mm), which fumes in the air.

Found %: C 21.98; 21.80; H 3.11; 3.17; Cl 47.93; 47.30; Si 13.05; 12.87. $C_4H_7O_2Cl_3Si$. Calculated %: C 21.69; H 3.18; Cl 48.01; Si 12.67.

Addition of $C_2H_5SiHCl_2$ to Vinyl Acetate. A mixture of 20 g of vinyl acetate, 52 g of $C_2H_5SiHCl_2$, and 1.2 g of benzoyl peroxide was heated as described for the reaction with $SiHCl_3$. Fractionation of the reaction mixture gave 52 g of a mixture of $C_2H_5SiHCl_2$ and vinyl acetate, 2 g of intermediate fractions, 9 g of nondistillable residue, and 5.3 g of 2-(dichloroethylsilyl)ethyl acetate as a colorless mobile liquid, b.p. 65° (2 mm), which fumed in the air.

Found %: C 33.76; H 5.60; Cl 32.60; Si 13.25. $C_6H_{12}O_2SiCl_2$. Calculated %: C 33.50; H 5.62; Cl 32.96; Si 13.04.

SUMMARY

1. A study was made of the reactions of CCl_4, $CHCl_3$, $SiCl_4$, $SiHCl_3$ and $C_2H_5SiHCl_2$ with vinyl acetate in presence of benzoyl peroxide.

2. It was shown that the yield of the product of equimolecular addition of CCl_4 to vinyl acetate increases with increase in the relative amount of CCl_4 taken. The yield of the product was improved, and its constants were determined with greater accuracy than previously.

3. Products of the equimolecular addition of $SiHCl_3$ and $C_2H_5SiHCl_2$ to vinyl acetate were prepared for the first time. It was shown that $SiCl_4$ does not react with vinyl acetate in presence of benzoyl peroxide under our conditions. When chloroform reacts with vinyl acetate a mixture of low-molecular-weight polymers is formed.

LITERATURE CITED

[1] M. S. Kharasch, E. V. Jensen, and W. H. Urry, J. Am. Chem. Soc. 69, 1100 (1947).

[2] C. A. Burkhard, and B. H. Krieble, J. Am. Chem. Soc. 69, 2687 (1947); L. H. Sommer et al., J. Am. Chem. Soc. 69, 188 (1947); E. W. Pietrusza, L. H. Sommer, and F. C. Whitmore, J. Am. Chem. Soc. 70, 487 (1948); A. I. Barry, L. De Pree, I. W. Gilkey and D. E. Hook, J. Am. Chem. Soc. 69, 2916 (1947); D. L. Baily and A. N. Pines, Ind. Eng. Chem. 46, No. 11, 2363 (1954).

[3] M. F. Shostakovskii, A. V. Bogdanova, M. M. Zverov and G. I. Plotnikova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 1236;* A. V. Bogdanova and M. F. Shostakovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 224.*

[4] M. et M-me Emile Levos, C. r. 230, 1669 (1950).

[5] R. Calas, Duffaunt and T. Valade, Bull. 6, 790 (1955).

[6] Russian Patent 44934 (1935); C. A. 4502 (1936).

[7] US Patent 396261 (1946).

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INVESTIGATION OF LACTONES AND LACTAMS

COMMUNICATION 10. ADDITION OF HYDROGEN SULFIDE TO N-VINYL LACTAMS

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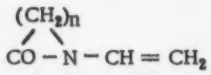
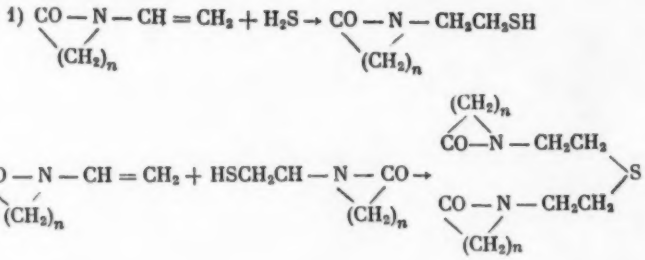
Addition at the double bond of N-vinyl lactams of general formula  has received hardly any attention in the literature; it has been the subject of detailed study in our laboratory. Investigation of some of the properties of N-vinylcaprolactam [2-oxo-1-vinylhexamethylenimine] and of 1-vinyl-2-pyrrolidinone showed that, like vinyl ethers, they are able to hydrolyze quantitatively by the ionic mechanism in an acid medium [1]. The addition of alcohols to N-vinylcaprolactam [2] resulted in the formation of only 8 % of the N-1-alkoxyethyl lactam; the process was complicated by side reactions. It is known that the addition of alcohols to alkyl vinyl ethers proceeds quantitatively [3]. The behavior of N-vinyl lactams in this reaction is closely analogous to that of vinyl sulfides, in particular ethyl vinyl sulfide [4]. The hydrohalogenation of N-vinyl lactams proceeds quantitatively, but the products are extremely unstable.

Hence, in reactions proceeding by an ionic mechanism, N-vinyl lactams behave appreciably differently from alkyl vinyl ethers. On the other hand, N-vinyl lactams polymerize readily in presence of free-radical catalysts such as H_2O_2 [5, 6] and 2,2'-azobis[2-methylpropionitrile] [7], which indicates their high tendency to undergo free-radical-induced reactions. In this connection we considered it to be of interest to study ways of synthesizing sulfur compounds from N-vinyl lactams on the basis of the addition of hydrogen sulfide by the free-radical mechanism. We previously [8-10] investigated this reaction for the case of vinyl ethers; we suggested the use of 2,2'-azobis[2-methylpropionitrile] as a universal catalyst for the anomalous addition of hydrogen sulfide and thiols to vinyl ethers of any structure [11].

We carried out the addition of hydrogen sulfide to N-vinylcaprolactam and 1-vinyl-2-pyrrolidinone in presence of this catalyst at ordinary and higher temperatures; in some experiments we used a medium of dioxane as solvent. As will be seen from Table 1 (experiments 2 and 6), the use of dioxane had no substantial effect on the course of the process. The effect of temperature was more notable; heating accelerated the process considerably (Table 1).

The reaction proceeds in two stages:



It was shown that for N-vinyl lactams reaction is much slower than for alkyl vinyl ethers; also, the relative rates of the two stages are different. Thus, in the case of alkyl vinyl ethers the first stage of the reaction is somewhat faster than the second and, by use of two- or three-fold excess of one of the reactants it is possible to dis-

place the process so that there is preferential formation of either the thiol or the sulfide [10, 11]. In the case of the N-vinyl lactams, a very great excess (of the order of 11-13 molecular proportions) of hydrogen sulfide was required in order to obtain the thiol, and even then the yield was low, the process being always accompanied by formation of the sulfide. It is evident that the second stage of the reaction is rapid, as compared with the slow first stage of addition of hydrogen sulfide to the N-vinyl lactam. This is shown clearly by the results given in Tables 1 and 2.

The free-radical reaction under consideration is very sensitive to the purity of the reactants. Oxidation products formed when the vinyl lactams are kept for a long time in contact with the air retard reaction appreciably, as they do also in the case of alkyl vinyl ethers [10, 12]. Thus, a sample of N-vinylcaprolactam which had been preserved for a long time gave no individual addition products in spite of the fact that it had been distilled immediately before the experiment. In experiments with 1-vinyl-2-pyrrolidinone it was difficult to achieve complete reproducibility of results: in all cases traces of the original substances remained and the course of the reaction was dependent on the carefulness with which the original 1-vinyl-2-pyrrolidinone was purified. We did not succeed in synthesizing the thiol from this compound in an adequately pure state and in a satisfactory yield: we synthesized it from 1-(2-chloroethyl)-2-pyrrolidinone and NaHS.

Difficulty was met in the separation of the reaction products. Vacuum fractionation resulted in decomposition: thus, in experiments with N-vinylcaprolactam we always obtained caprolactam as the main decomposition product. An extraction method of separating the products was developed. It is interesting that in all experiments with N--vinylcaprolactam we isolated small amounts of caprolactam hydrosulfide when the reaction mixture was diluted with ether. We did not detect any analogous product in experiments with 1-vinyl-2-pyrrolidinone; neither did we observe decomposition with elimination of the vinyl group.

The synthesized thiols were fairly viscous clear colorless liquids which could be vacuum-distilled without decomposition; they were soluble in all organic solvents. The sulfides were crystalline solids, having well-defined melting points and dissolving readily in all organic solvents and partially in water-ether mixtures. The synthesized sulfides and thiols were peculiar in their behavior toward alcoholic mercuric chloride. Instead of the formation of the usual complex compounds in the case of sulfides and chloromercury derivatives in the case of thiols, complete decomposition of the organic molecule occurred, and the precipitates obtained, both from thiols and from sulfides, contained the same, very low percentage of carbon. In both cases decomposition occurred with liberation of HCl.

EXPERIMENTAL

N-Vinylcaprolactam: b.p. 116-117° (10 mm); 95° (4 mm); n_D^{20} 1.5130. 1-Vinyl-2-pyrrolidinone: b.p. 78-79° (6 mm); 65-64.5° (2 mm); n_D^{20} 1.5120 [15]. The work was carried out with liquid hydrogen sulfide by the procedure described in detail previously [10]. Weighed amounts of the catalyst, the N-vinyl lactam, and in some experiments the solvent were introduced into a tared ampoule having a constriction. Hydrogen sulfide was condensed in the ampoule, and when the required weight was attained the ampoule was sealed, generally under a vacuum, though in some experiments with N-vinylcaprolactam sealing was carried out without evacuation; no substantial difference was observed. Ampoules containing a large excess of hydrogen sulfide were transferred while still cold into an autoclave, into which nitrogen was passed from a cylinder to a pressure of 15-16 atm so as to equalize pressures. When heating was applied during reaction, the ampoules were placed in metal jackets and heated in a water thermostat. After the reaction the ampoules were transferred carefully to a Dewar vessel containing liquid nitrogen and were opened in the chilled state. Excess of hydrogen sulfide was allowed to evaporate, and the reaction mixture was treated further as indicated below.

I. Reaction of Hydrogen Sulfide with N-Vinylcaprolactam

The results of the series of experiments in which treatment was by the extraction method are given in Table 1. We now describe one experiment for each method of treating the reaction mixture.

a) Separation of Products by Fractional Distillation. Experiment 1. Reaction was between 8 g of N-vinylcaprolactam and 2.7 g of hydrogen sulfide (1 : 1.4 moles) in presence of 0.02 g of 2,2'-azobis[2-methylpropionitrile]. After seven days, including 43 hours of heating at 60°, the ampoule was opened; increase in weight 2 g. The reaction mixture was fractionated from a flask with a sword-shaped side arm. The products were Fraction I, b.p. 123-126° (4-4.5 mm), 3 g; residue in the flask, 5.8 g (resin). Fraction I rapidly solidified and was found to

be 6-caprolactam; a mixture test with known caprolactam showed m.p. 70°, i.e. there was no depression.

It was found, therefore, that vacuum fractionation is accompanied by decomposition and does not result in the isolation of individual sulfur compounds.

TABLE 1

Addition of Hydrogen Sulfide to N-Vinylcaprolactam

(catalyst 0.2 % by weight)

Experiment	Amount H_2S (moles/mole vinyl lactam)	Duration of experiment: Total (days)	Duration of experiment: Heating (hours) (temp. °C)	Yields of reaction products: $CO(CH_2)_5NH \cdot H_2S$ (g)	Thiol (%)	Sulfide (%)	Total (%)
2*	1.4	13	43 (60)		4	87.9	91.9
6*	11.4	27	— (20)	0.1	43.3	39.2	82.5
3	0.9	25	— (20)	0.2	6.1	72.3	85.4
4	3.3	17	— (20)	0.1	14.6	61.8	76.3
7**	13.4	15	— (20)	Absent	No indiv. product isolated		
8	1.2	13	55 (60)	0.1	3.1	84.5	87.6
9**	1.2	13	55 (60)	Absent	No indiv. product isolated		
10**	13.3	30	— (20)	»	»	»	»
11	14.6	30	— (20)	0.1	41.1	44.2	85.3
13	1.0	7	35 (60)	0.1	4.8	82.6	87.4

* In Experiments 2 and 6 dioxane was used as solvent.

** In Experiments 7, 9, and 10 the vinylcaprolactam used had been kept a long time and was distilled before the experiment.

b) Separation of Products by the Extraction Method. In those experiments in which dioxane was used as solvent, it was first distilled off under reduced pressure and the reaction mixture was diluted with ether. Experiment 11. Reaction was between 12.3 g of N-vinylcaprolactam and 44 g of hydrogen sulfide (1 : 14.6 moles) in presence of 0.03 g of catalyst. The ampoule was opened after it had stood for 30 days at 17-20°. The reaction mixture was diluted with ether, and a white powder was precipitated in flocs. It was filtered off (0.1 g), washed repeatedly with ether, and dried to constant weight in a vacuum desiccator. The substance was insoluble in organic solvents and was infusible; it corresponded in analysis to caprolactam hydrosulfide $CO(CH_2)_5NH \cdot H_2S$

Found %: C 48.78; 48.88; H 8.86; 8.94; S 21.27; 21.53; N 9.69; 9.66. $C_6H_{13}ONS$. Calculated %: C 48.94; H 8.90; S 21.78; N 9.51.

The ether solution was treated with 10 % KOH solution. The ether layer was separated, washed with water, and dried with freshly calcined sodium sulfate. When ether was removed the product crystallized in long needles; the weight of this sulfide fraction was 6.1 g (44.2 %). After being washed several times with ether and pressed out on a porcelain tile, the crystals of N,N'-(2,2'-thiodiethyl)dicaprolactam melted at 83°.

Found %: C 61.34; 61.61; H 8.89; 9.04; S 10.33; 10.27; N 8.91; 9.01. $C_{16}H_{28}N_2O_2S$. Calculated %: C 61.50; H 9.03; S 10.26.

The aqueous alkaline layer that remained was treated with 1 N HCl, and the thiol liberated was extracted with ether; the extract was washed with water and dried. Removal of ether left 6.9 g (41.1 %) of thiol fraction. After two fractionations it had constant properties: b.p. 113-114° (2.5 mm); n_D^{20} 1.5254; d_4^{20} 1.1019; found MR 48.22; calculated MR 48.58; it was N-(2-mercaptoethyl)caprolactam:

$$CO(CH_2)_5N-CH_2CH_2SH$$

Found %: C 55.62; 55.25; H 8.64; 8.55; S 18.46; 18.50; N 8.30; 8.42. $C_8H_{15}ONS$.
Calculated %: C 55.45; H 8.73; S 18.51; N 8.08.

Experiment 7. This was carried out on a sample of N-vinylcaprolactam that had been kept for a long time. The conditions are shown in Table 1. The reaction mixture was treated by the extraction method. No caprolactam hydrosulfide was present. The supposed sulfide fraction (6.5 g) was found to be a polymeric product of low molecular weight which did not contain sulfide. The thiol fraction (12 g) was fractionated three times; much resinification occurred, and 6 g of a wide fraction, b.p. 120-127° (4 mm) was obtained which solidified in the receiver. In admixture with known caprolactam this substance melted at 70°. In this case, therefore, the decomposition product caprolactam was formed.

II. Reaction of Hydrogen Sulfide with 1-Vinyl-2-pyrrolidinone

The results of some experiments are given in Table 2. In these experiments the products were separated by the extraction method, although the treatment was complicated in this case by the somewhat higher solubility of the sulfur compounds prepared from 1-vinyl-2-pyrrolidinone. It was found that the liquid separated from the mass of crystals of the sulfide fraction gave the iodoform reaction [13] characteristic of N-vinyl lactams. It is probable that traces of unchanged 1-vinyl-2-pyrrolidinone remained. Vacuum fractionation was again found to be not very satisfactory.

TABLE 2

Addition of Hydrogen Sulfide to 1-Vinyl-2-pyrrolidinone

(catalyst 0.2% by weight)

Experiment	Amount H_2S (moles/ mole vinyl lactam)	Duration of experiment		Yields of reaction products		
		Total (days)	Heating (hours) (temp.°C)	Thiol (%)	Sulfide (%)	Total (%)
1	3	20	— (20)	—	73.4	73.4
3	12.5	27	— (20)	10.4	63.8	74.2
5	1.24	9	35 (60)	7.1	64.5	71.9
6	1.2	19	— (20)	—	87	87
7	12.4	12	— (20)	8.5	71.3	79.5
8	12.3	21	— (20)	5.7	80.8	86.5

Experiment 1. The conditions of the experiment are given in Table 2. After being diluted with ether, the reaction mixture was treated with 10 % KOH solution. It was then found that the sulfide fraction also passed into the alkaline extract; the ether layer contained hardly any sulfide. The alkaline solution was treated with 1 N HCl, and the thiol fraction was extracted with ether; 1.71 g of substance having thiol properties was isolated from it. Water was vacuum-distilled in the cold from the salt solution; the dry residue was extracted with ether, and after distillation there remained 9.5 g of substance, which crystallized after one day. The crystals had the form of rectangular plates, m.p. 101.5°; they consisted of 1,1'-(2,2'-thiodiethyl)di-2-pyrrolidinone; yield 73.4 %.

Found %: C 56.15; 56.23; H 7.79; 7.81; S 12.69; 12.41; N 10.75; 10.58. $C_{12}H_{20}N_2O_2S$
Calculated %: C 56.22; H 7.86; S 12.51; N 10.93.

Experiment 2. Reaction was between 10.4 g of 1-vinyl-2-pyrrolidinone and 9 g of hydrogen sulfide (1 : 2.9 moles) in presence of 0.02 g of 2,2'-azobis[2-methylpropionitrile]. After 24 days at 17-20° the ampoule was opened; the increase in weight was 2.2 g. Three fractionations, which were accompanied by resinification of the reaction mixture, gave:

Fraction I, b.p. 75-80° (4 mm); 0.9 g; n_D^{20} 1.5200

Fraction II, b.p. 80-110° (4 mm); 0.4 g; n_D^{20} 1.5275

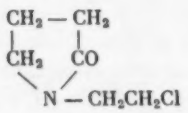
Fraction III, b.p. 191-193° (3.5 mm); 3.1 g.

a highly viscous dark-yellow substance.

After refractionation Fraction I had b.p. 73-74° (3 mm) and n_D^{20} 1.5120; it was unchanged 1-vinyl-2-pyrrolidinone. When seeded with a crystal of the known sulfide, Fraction III crystallized. After being washed as in Experiment 1, the crystals melted at 101.5°. Hence, we succeeded in isolating some sulfide fraction by fractionation, but considerable losses occurred.

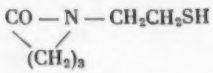
Synthesis of 1-(2-Mercaptoethyl)-2-pyrrolidinone

We synthesized 1-(2-mercaptoethyl)-2-pyrrolidinone from 1-(2-chloroethyl)2-pyrrolidinone and NaHS by a method similar to that used by Bennet [14] for the preparation of 2-mercaptoethanol. The chloro compound used



had the following properties: b.p. 119-121° (7.3 mm); n_D^{18} 1.4968. The experiment was carried out in an apparatus provided with a stirrer. Crystalline $Na_2S \cdot 9H_2O$ (26 g) was fused in a water bath (80-90°), and a powerful stream of hydrogen sulfide was passed for ten minutes, when the solution became colorless. It was cooled to 50°, and 15 g of the chloro compound was added from a dropping funnel over a period of 15-20 minutes. A copious precipitate of salt was formed. Stirring of the reaction mixture was continued at 50-60°, and a powerful stream of hydrogen sulfide was passed. When cold the contents of the flask were treated with 14 ml of glacial acetic acid; the liquid was poured into a separating funnel, and the precipitate was extracted with ether several times, the extracts being added to the liquid in the funnel. The liquid was dried and ether was distilled off; the weight of the residue was 13 g. Vacuum fractionation gave a main fraction of b.p. 125-127° (4.5 mm); n_D^{20} 1.5290; 9 g.

After a second fractionation the constants of the substance did not change further: b.p. 123-124° (3.5-4 mm); 118-119° (2 mm); 131-132° (5.5 mm); n_D^{20} 1.5300; d_4^{20} 1.1469; found MR 39.35; calculated MR 39.11. The substance, which was obtained in 61 % yield, was 1-(2-mercaptoethyl)-2-pyrrolidinone



Found %: C 49.24; 49.26; H 7.55; 7.53; S 21.96; 21.84. $C_6H_{11}ONS$. Calculated %: C 49.62; H 7.64; S 22.08.

Action of Alcoholic Mercuric Chloride on the Sulfide and the Thiol

A 20 % alcoholic solution of mercuric chloride was added to an alcoholic solution of the sulfide or thiol prepared from N-vinylcaprolactam. When the mixture was warmed, a yellowish precipitate formed which gradually became cream in color. In both cases the supernatant solution was acid to Methyl orange. The precipitate was filtered off, washed with alcohol and ether, and brought to constant weight in a vacuum desiccator; in each case it was infusible. Results of microanalysis:

Sulfide sample	Thiol sample
C (%): 3.65, 3.76	C (%): 3.69, 3.48
H (%): 0.80, 0.83	H (%): 0.98, 0.84

SUMMARY

1. The free-radical-induced addition of hydrogen sulfide to N-vinyl lactams was studied, and it was shown that sulfides and thiols can be prepared from N-vinylcaprolactam and 1-vinyl-2-pyrrolidinone in this way in overall yields of 75-85 %.

2. It was shown that the second stage of the process is the faster, so that the sulfide is preferentially formed. Synthesis of the thiol from N-vinylcaprolactam in 40-45 % yield was effected by the use of an 11-13-fold molar excess of hydrogen sulfide.

3. It was shown that the addition of hydrogen sulfide to N-vinylcaprolactam is retarded when the latter is kept for a long time in contact with air.

4. The synthesis of a thiol having a pyrrolidinone ring was carried out in 60 % yield by the reaction of 1-(2-chloroethyl)-2-pyrrolidinone with NaHS.

LITERATURE CITED

[1] M. F. Shostakovskii, F. P. Sidel'kovskaia and M. G. Zelenskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 689.*

[2] M. F. Shostakovskii and F. P. Sidel'kovskaia, J. Gen. Chem. 24, 1576 (1954).*

[3] M. F. Shostakovskii and N. A. Gershtein, J. Gen. Chem. 16, 937 (1946); Bull. Acad. Sci. USSR, Div. Chem. Sci. 1948, 453; J. Gen. Chem. 18, 451 (1948).

[4] M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 154.*

[5] M. F. Shostakovskii and F. P. Sidel'kovskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 108.*

[6] M. F. Shostakovskii, N. A. Medzykhovskaia, and M. G. Zelenskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 682.*

[7] M. F. Shostakovskii, F. P. Sidel'kovskaia, and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 919.*

[8] M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 438, No. 5, 560.

[9] M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 478.*

[10] M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 292, 303.*

[11] M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 734.*

[12] M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 357.*

[13] M. F. Shostakovskii, F. P. Sidel'kovskaia, and M. G. Zelenskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 615.*

[14] G. M. Bennet, Soc. 119, 422 (1921); 2139 (1922).

[15] M. F. Shostakovskii, F. P. Sidel'kovskaia, and M. G. Zelenskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1457.*

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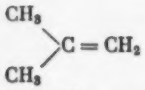
RAMAN INVESTIGATION OF THE STRUCTURE OF LOWER ISOBUTENE POLYMERS

M. I. Batuev, A. P. Meshcheriakov and A. D. Matveeva

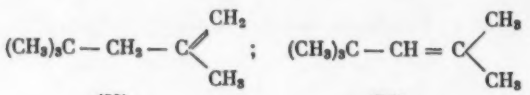
The tendency for isobutene to polymerize, which was discovered by Butlerov, was later studied by Butlerov himself [1], Vagner [2], Prilezhaev [3], El'tekov [4], Lebedev [5], Whitmore [6], Petrov [7], Topchiev [8], and others. The polymerization of isobutene



(I)

occurs both when it is heated in absence of catalysts [5], and under the action of various acid catalysts (sulfuric acid, fuller's earth, boron trifluoride etherate $(C_2H_5)_2O \cdot BrF_3$, $ZnCl_2$, and others). The polymerization of isobutene is a reversible process [5] whose course and rate are dependent on many conditions: temperature, nature and amount of catalysts, added substances, solvents, etc. At 200° and above, depolymerization predominates and, at the best, only dimers and trimers are formed under such conditions. Under special conditions the polymerization of isobutene can be effected stepwise with formation of the lower polymers [5]. In low-temperature catalytic polymerization (at -80° and below), reaction, which is very vigorous and is almost complete in a fraction of a second, proceeds with the evolution of much heat and the formation of linear polymers; according to the most recent results, the molecular weight of these polymers may attain 500,000 and more.

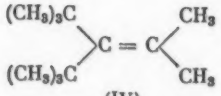
The dimer of isobutene "diisobutene" was investigated in detail by Butlerov [1], Vagner [2], and Prilezhaev [3]. They showed that it is a mixture of two isomers (II) and (III) [5] with a predominance of (II) [9]:



(II) (III)

Later, the Raman spectra of the two individual isomers were determined [10], and also of the mixture of the isomers (II) and (III) [11]. Comparison of the intensities of the double-bond frequencies led to the conclusion that diisobutene consists of 76 % of the isomer (II) and only 24 % of the isomer (III). These data are in accord with Whitmore's chemical results [12], which indicate about 80 % of (II) and about 20 % of (III). According to [10], the vibration frequency of the double bond of (II) (1648 cm^{-1}), in which the double bond is at the end of the chain, is lower than that of the double bond of (III) (1667 cm^{-1}), in which the double bond is not at the end.

The trimer of isobutene, "triisobutene," was isolated by Butlerov in a form which he regarded as a single isomer of structure:

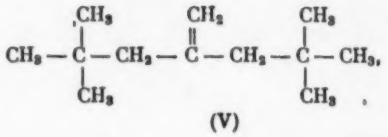


(IV)

This isomer has not been prepared and has not been identified in the trimer fraction from isobutene. Lebedev and

Koblianskii [5] showed that the trimer fraction isolated by Butlerov actually consisted of a preponderating low-boiling part (179-181°, corrected) and a very small amount of high-boiling material (195-196°, corrected), but they did not establish the structures of the triisobutene isomers.

As a result of extensive chemical investigations, Whitmore and coworkers [6] concluded that the low-boiling part of the trimer fraction consists of the isomers (V) and (VI) and the high-boiling part of the isomers (VII) and (VIII):



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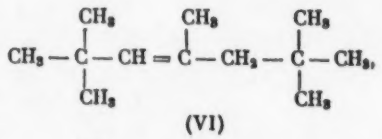

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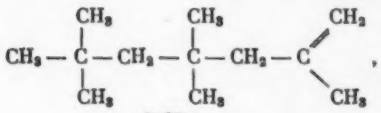
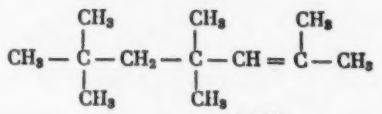


(VII)



(VIII)

The relative amounts of the four isomers in the trimer fraction are as follows [6]: (V) : (VI) : (VII) : (VIII) = = 54 : 36 : 5 : 5, i.e. according to Whitmore the two low-boiling isomers form the bulk (90 %) of the trimer fraction. This result has been confirmed in the work of other authors [13].

The structure of the tetramer, and still more of the higher polymers, has not been determined chemically. Only suggestions of their possible structures have been made on the basis of the very limited data available.* Lebedev advanced and experimentally confirmed the view that there is a predominance of polymer forms that are inactive for further polymerization in the lower fractions starting from the trimer fraction, as distinct from the dimer fraction, in which the active isomer (II) is predominant, and, of course, from the extremely active monomer (I).

It follows from these considerations that isomers of the types (V) and (VI) are inactive trimer forms, which are excluded from further polymerization and therefore accumulate in the lower fractions. Linear-chain polymerization proceeds, both in a monomer and in a dimer medium, through high-polymer forms of the type (VII) [5]; at higher stages of polymerization the process is interrupted by the formation of inactive forms of types such as (V) and (VI).

Papers have been published recently by Gross, Nel'son, Slobodin, and Markova [15] in which, mainly on the basis of Ramanspectrum data (determination of the position of the double bond in the molecule by the Raman spectrum method), views are advanced which conflict with the results of chemical and Raman investigations given above. Thus, these authors, on the basis of the relative intensities of the two double-bond frequencies in their Raman spectrum of diisobutene,** found that there is no marked predominance of the isomer (II) in this fraction, the amounts of the two isomers being approximately equal.

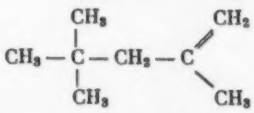
In the trimer fraction of isobutene polymerizate obtained in presence of fuller's earth, Gross and coworkers found two frequencies, 1636 and 1652 cm^{-1}, which in their opinion arise by splitting of the frequency 1644 cm^{-1} as a result of Fermi resonance or rotation isomerism, and also the higher frequency 1671 cm^{-1}. Taking account of results [10] which indicate that the low double-bond frequency (which is split into two, according to Gross and coworkers, in the trimer) is associated with the diisobutene isomer (II) with the double bond at the end of the chain and the higher frequency with the isomer (III) with the double bond in the middle of the chain, Gross and coworkers concluded from their results that "the triisobutene formed by polymerization consists both of compounds having the double bond at the end of the chain and also of compounds having the double bond in the middle of the chain .... From the relative intensities of the double-bond frequencies it must be concluded that isomers having the double

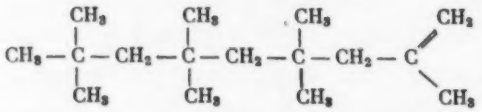
* It should be noted that attempts to determine the structures of isobutene polymers by degradation under severe conditions are unlikely to give any direct information on the structures of the skeletons of the original polymers, for the resulting fragments of the polymer can undergo various transformations during the degradation process. Any conclusions made on the basis of this method can only be very tentative [14].

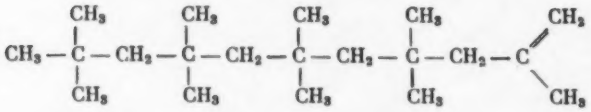
** Diisobutene was obtained by Gross and coworkers by the polymerization of isobutene monomer in presence of sulfuric acid.

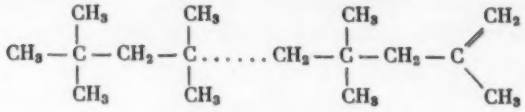
bond in the middle of the chain are present in the smaller amount" [15].

The isomer with the double bond at the end of the chain is regarded by Gross and coworkers to be isomer (II) in the case of the dimer, isomers (IX) and (X) for the tetramer and pentamer, and, in general only isomers of type (XI) for isobutene polymers:



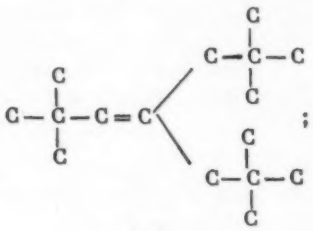




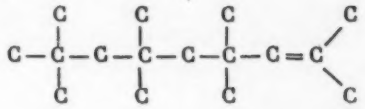


The reader of their papers is therefore justified in concluding that by the trimer with the double bond at the end of the chain they understand only the isomer (VII). In this case, the conclusion of Gross and coworkers to the effect that the trimer fraction consists mostly of the isomer with the double bond at the end of the chain is in sharp contradiction with the above-cited results of chemical investigations by other authors.

From the tetramer fraction onward,* Gross and coworkers could no longer detect the higher double-bond frequency in the region of 1670 cm^{-1}, but only the lower frequency, which was again split into two (1636 and 1652 cm^{-1}); they concluded that the tetramer fraction consists almost entirely of the isomer with the double bond at the end of the chain, namely the isomer (IX). On the basis of this evidence, therefore, they consider that their own tentative suggestion of the presence of not only (IX), but also the two isomers



(XII)



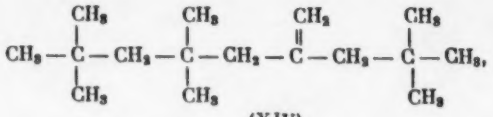
(XIII)

in the tetramer fraction, must be rejected. However, taking account of the inaccuracy of the method, Gross and coworkers conceded that the isomers (XII) and (XIII) might be present in an amount of not more than 5 %, which would be practically undetectable.

In the case of the tetramer, the authors tried to prove the structure that they assigned to it (IX) by chemical means: they investigated the ozonolysis products of their tetraisobutene. They write [15]: "The chemical results are in full accord with the results obtained from Raman spectra." However, we can show immediately that their chemical proof is not unequivocal: the formic acid, 2,2-dimethylpropionic acid, formaldehyde, and ketone of molecular weight 230 (the authors did not determine its structure) which they isolated could have been obtained

* In the polymerization of isobutene over fuller's earth, Gross and coworkers obtained trimer, tetramer, and pentamer fractions and a polymer of molecular weight 800.

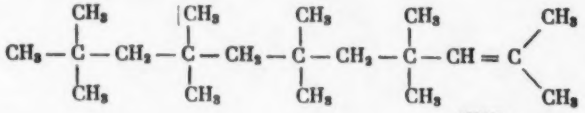
also by the ozonization of a tetraisobutene of different structure, e.g.



(XIV)

which was not even mentioned among the possible structures that they suggested.

As regards the pentamer fraction, Gross and coworkers assume (" on the basis of considerations of chemical structure" [15]) that only two forms (X) and (XV) can be present:



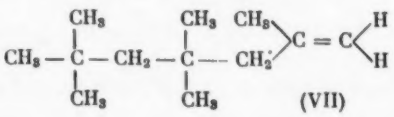
(XV)

Gross and coworkers found only the two low frequencies 1640 and 1649 cm^{-1} (in their opinion formed as a result of the splitting of the frequency 1644 cm^{-1}, see above) in the Raman spectrum of the pentamer fraction, and the higher frequency of about 1670 cm^{-1} could not be detected at all; they asserted, therefore, that within the limits of accuracy of the method (about 5 %) "in the polymerization process the isobutene pentamer is obtained in the form corresponding to the structure (X), i.e. with a double bond at the end of the polymer chain" [15]. In the case of the polymer of average molecular weight 800, Gross and coworkers assume only the form (XI) with the double bond at the end of the chain, for again they observed the low double-bond frequency split into two (1637, 1650 cm^{-1}), which is characteristic for the form (XI); the higher frequency of about 1670 cm^{-1}, which is characteristic for other forms in which the double bond is in the middle of the chain, was not observed at all.

Hence, according to Gross and coworkers, in the dimer fraction the isomer with the double bond at the end of the chain (II) is present in an amount almost equal to that of the isomer with the double bond in the middle of the chain (III), in the trimer fraction the form with the terminal double bond is already the major component, and from the tetramer fraction onward it is, for practical purposes, the only component present [(IX), (X), and (XI)]. However, according to the chemical and Raman spectrum results of other authors discussed at the commencement of this paper, the form (II) greatly predominates in the dimer fraction, the trimer fraction consists predominantly of the inactive forms (V) and (VI), and not (VII), and the subsequent low fractions consist also of analogous inactive forms, but not (IX), (X), and (XI), which are very active in further polymerization and are therefore converted into higher polymers. On the contrary, according to Gross and coworkers, both in the lower (beginning with the trimer) and in the higher fractions forms of the type (XI), which are active in further polymerization, predominate; more accurately, from the tetramer fraction onward practically only these forms [(IX, (X), and (XI)] are present, none of the others being detectable (within the limits of the accuracy of the experiment).

It should be noted that, in its application to the isomers of the isobutene polymers, the terms "isomer with the double bond at the end of the chain" and "isomer with the double bond in the middle of the chain" are not very apt and can be misleading, particularly when they are written out in schematic form as in the case of structures (V)—(VIII). When they are written in this way, it is easy to suppose that the only isomer of these four which has a double bond at the end of the chain is the form (VII) [which is analogous to the forms (II), (IX), (X), and (XI)] and that there is no other of the same type, so that only this one has the lower double-bond frequency of 1644 cm^{-1} (which, according to Gross and coworkers, is split into two: 1637 and 1652 cm^{-1}).

Actually, isomers of the type (XI) [(II), (VII), (IX), (X), etc.] and the types (V), (XIV), etc. are all asymmetric dialkylethylenes in which the position of the double bond in the molecule is always the same in type, as can be seen when the formulas of these compounds are written as follows:



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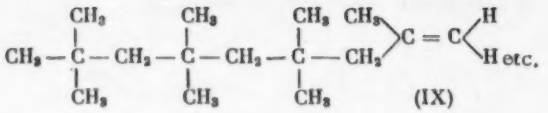
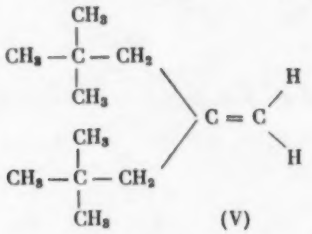
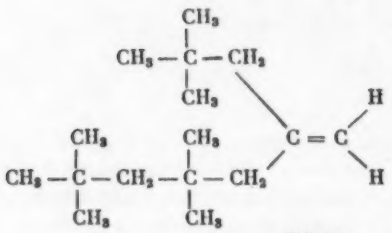


(IX)

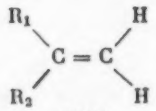


(V)



(XIV)

The difference between isomers of the type (XI) [(II), (VII), (IX), and (X)] and isomers of the type (V) and (XIV) is that in the first



(XVI)

R_1 is always CH_3 and R_2 is a longer-chain alkyl, whereas in the second both R_1 and R_2 are alkyls of longer chain length than methyl. Experiment shows, however, that any difference in the alkyls R_1 and R_2 in molecules of type (XVI) has no substantial effect on the region of the double-bond frequencies; for these compounds this region lies at about 1650 cm^{-1}. The double-bond frequencies characteristic for isomers of the type (XI) [(II), (VII), (IX), and (X)] are close to the frequencies for isomers of the type (V) and (XIV). From this it already follows that the detection of these frequencies in the trimer, tetramer, and other fractions of the isobutene polymerizate in accordance with the above-cited experimental data of Lebedev and Whitmore and coworkers may be evidence of the predominance of isomers of the type (V) and (XIV) etc., rather than of the type (XI) [(VII), (IX), and (X)].

EXPERIMENTAL

We determined the Raman spectra of the dimer, trimer, and tetramer fractions of the isobutene polymerizate.* The spectra were determined with a Soviet ISP-51 three-prism spectrograph having a central camera; the exciting radiation was from the mercury line 4358 A. Three of the spectra are given below.

Raman Spectra of Isobutene Polymers

Diisobutene [b.p. 100-101° (742.5 mm)], $\Delta\nu$ (cm^{-1}): 127 (2), 135 (0), 186 (2•), 199 (2•), 293 (3••), 307 (3••), 314 (3••), 331 (3••), 380 (3•), 390 (3•), 463 (1), 501 (0), 565 (4 db), 688 (6), 769 (8), 828 (3db), 893 (3•), 909 (6•), 925 (2•), 936 (6•), 1002 (1), 1029 (0), 1047 (1), 1076 (0), 1102 (1), 1155 (5b), 1203 (5), 1239 (5), 1257 (0), 1269 (1), 1300 (1), 1328 (1), 1352 (0), 1384 (1•), 1394 (0•), 1412 (6), 1447 (8•), 1466 (2•), 1643 (8), 1668 (2), 2710 (2), 2909 (10• b), 2930 (2•), 2959 (9• b), 2981 (3• b), 3005 (1), 3021 (1), 3076 (3).

* Work on chemical aspects associated with the Raman spectrum investigation of the structure of the lower isobutene polymers [15] is being continued by one of us, A. P. Meshcheriakov.

Triisobutene [before oxidation; low-boiling fraction, b.p. 176-176.8° (730 mm)], $\Delta\nu$ (cm^{-1}): 186 (4*), 202 (1*), 224 (0), 239 (3*), 254 (3*), 281 (2**), 295 (2**), 328 (3), 353 (1), 388 (1), 413 (1), 453 (6*), 467 (2*), 497 (2), 528 (3), 680 (7), 739 (5), 766 (8), 904 (4*), 916 (4*), 933 (5*), 1008 (1**), 1030 (1**), 1096 (2*), 1168 (5*), 1200 (6* b), 1234 (7), 1260 (0), 1285 (5), 1409 (5), 1448 (8*), 1468 (4*), 1640 (6**), 1654 (7**), 2710 (3), 2864 (5* b), 2904 (9* b), 2931 (2*), 2958 (9* b), 2981 (5*), 3004 (0), 3024 (0), 3076 (3).

Tetraisobutene [before oxidation; low-boiling fraction obtained over $ZnCl_2$, b.p. 106-107° (8 mm)], $\Delta\nu$ (cm^{-1}): 184 (1), 208 (0), 250 (3 b), 299 (3 b band), 353 (0*), 377 (0*), 395 (0*), 418 (0*), 483 (0), 523 (3 b), 547 (0), 575 (3 b), 726 (3*), 743 (10*), 768 (2), 911 (4*), 931 (6*), 956 (0), 982 (0), 1032 (0), 1107 (3 b), 1152 (3*), 1175 (3*), 1201 (4), 1231 (6*), 1247 (4*), 1284 (3), 1320 (3), 1362 (0), 1410 (3), 1445 (10**), 1470 (5**), 1640 (6*), 1656 (6*), 2711 (3), 2841 (2*), 2868 (3*), 2904 (10*), 2932 (1*), 2956 (10*), 2983 (1*), 3074 (1).

Intensities are given on a ten-grade visual scale. The letters given with the intensities denote: b, broad line; db., double line. The asterisks given with the intensities indicate lines disposed on a background that is common to neighboring lines marked with the same number of asterisks.

Diisobutene was prepared by the polymerization of isobutene in presence of dilute sulfuric acid. From the ratio of the intensities of the two frequencies 1643 and 1668 cm^{-1} observed in the spectrum, of which the first is to be attributed to the isomer (II) and the second to the isomer (III), it was found that the mixture contains 80 % of the isomer (II) and 20 % of the isomer (III), which is in accord with Raman spectrum [10, 11] and chemical [12] data, but does not confirm the Raman spectrum results of [15]. In the diisobutene spectrum, no lines other than those attributable to the isomers (II) and (III) [10] were detected.

Triisobutene was prepared by the polymerization of isobutene in presence of 63 % sulfuric acid. The low-boiling [176-176.8° (730 mm)] and high-boiling [182-183° (765 mm)] parts of the trimer fraction were collected separately in fractionation through a column of 38 theoretical plates. We then oxidized the low-boiling fraction; if it really did contain the two isomers (V) and (VI), then, according to Prilezhaev's rule,* the isomer (VI) should be oxidized preferentially. Distillation of the oxidation products should then result in considerable enrichment of the fraction in (V), which is bound to be manifested in the Raman spectrum of the fraction.

In order to attain more complete oxidation of the low-boiling part of the trimer fraction, we used three different sets of conditions of progressively increasing degree of severity: 1) treatment with $KMnO_4$ in an alkaline medium (KOH) at 100° (water bath); 2) treatment with $K_2Cr_2O_7$ in an acid medium (excess of 60 % sulfuric acid) at room temperature; 3) oxidation in an alkaline medium (as in the first treatment) followed by oxidation in an acid medium (as in the second treatment).

The yield of the high-boiling part of the trimer fraction was very small and it was therefore not oxidized. The lowness of the yield of the high-boiling fraction confirms Lebedev and Whitmore's results concerning the great predominance of the isomers (V) and (VI), which are inactive in polymerization, in the trimer fraction to the exclusion of the isomer (VII), thought to be present by Gross and coworkers. The latter investigated the trimer fraction as a whole (the boiling range of the fraction was not indicated). In the region of double-bond frequencies in the spectrum of this fraction they found three lines: 1636, 1652, 1671 cm^{-1}. In the spectrum of the unoxidized low-boiling part of our trimer fraction we found only two frequencies, 1640 and 1654 cm^{-1}, and in the unoxidized high-boiling fraction three frequencies: 1640, 1653, and 1670 cm^{-1}. This indicates that, unlike Gross and coworkers, we succeeded in separating low-boiling isomers of the first fraction characterized by double-bond frequencies of 1640 and 1654 cm^{-1} from the high-boiling isomer (VIII) characterized by the frequency 1670 cm^{-1}. The frequencies 1640 and 1653 cm^{-1} of the second fraction can be attributed to the isomers (V) and (VI) of the low-boiling fraction which distilled over partially in the second, high-boiling fraction; but they may be attributed also to other high-boiling isomers in the second fraction, particularly to (VII). The content of the isomer (VIII) in the whole trimer fraction, as judged by the intensities of the double-bond frequencies, is extremely small — clearly only a few percent (less than 10 %).

Double-bond Frequencies in Triisobutene Fractions (cm^{-1})

Low-boiling fraction [176-176.8° (730 mm)]: 1640, 1654

High-boiling fraction [182-183° (765 mm)]: 1640, 1653, 1670.

* According to Prilezhaev's rule for the oxidation of alkenes, in the oxidation of di- and tri-substituted ethylenes the latter are oxidized considerably more rapidly than the former [16].

We investigated also the spectra of the three oxidized (under three different sets of conditions, as indicated above) samples of the low-boiling trimer fraction after removal of oxidation products by distillation. It was found that the intensity of the line 1653 cm^{-1}, as also that of the line 739 cm^{-1}, became rapidly lower as the oxidation of the fraction became progressively more severe.

These experimental results clearly show that the doublet 1640, 1654 cm^{-1} does not arise from Fermi resonance or rotation isomerism,* as was supposed by Gross and coworkers; they indicate, in fact, that the low-boiling part of the trimer fraction contains the two isomers (V) and (VI). From this mixture, by preferential oxidation of the isomer (VI) and removal of oxidation products by distillation, the isomer (V) can be isolated in an almost pure state.

TABLE

Relative Intensities of Some Frequencies of the Low-boiling Fraction of Triisobutene Oxidized to Different Extents

Oxidation treatment	Frequency (cm^{-1})		
	739	1640	1654
1. Before oxidation	5	6	7
2. After oxidation in an alkaline medium	4	6	6
3. After oxidation in an acid medium	2	6	3
4. After the double oxidation	1	6	1

In accordance with the results of the chemical investigations of Lebedev and Whitmore discussed above, we may state that in the double-bond region the isomer (V) is characterized by the frequency 1640 cm^{-1}, the isomer (VI) by the frequency 1654 cm^{-1}, the isomer (VII) by a frequency coinciding with that for the isomer (V) (1640 cm^{-1}), the isomer (VIII) by the frequency 1670 cm^{-1}. It is, of course, possible that other triisobutene isomers may be present in small amount, their frequencies being either coincident with those cited or indistinguishable against the general background of these frequencies.

Tetraisobutene (diisobutene dimer) was prepared by reaction of 2-chloro-2,4,4-trimethylpentane with diisobutene in presence of $ZnCl_2$ at room temperature. The product was distilled through the 38-plate column and the 106-107° (8 mm) fraction was collected. This fraction was oxidized with the same object as in the case of the trimer fraction [it was first oxidized with alkaline $KMnO_4$ at 100° (water bath) and then with $K_2Cr_2O_7$ in excess of 60 % sulfuric acid at room temperature; the oxidation products were then distilled off].

In the spectra of these two fractions (unoxidized and oxidized), no frequency of about 1670 cm^{-1} could be detected in the double-bond region, i.e. isomers of the type (XII) and (XIII) were absent (within the limits of experimental error). In the unoxidized fraction two frequencies, 1640 and 1656 cm^{-1}, were found. These two frequencies were still present in the oxidized fraction, but the intensity of the second was greatly reduced; just as in the trimer fraction oxidation led to increase in the concentration of the isomer (V), so in the tetramer fraction it led to increase in the concentration of the analogous isomer (XIV).

We prepared a tetramer fraction also by the polymerization of isobutene in presence of 3 % by volume of sulfuric acid at a temperature of from -15° to +20°. This fraction was refractionated through the 38-plate column into two : 84-90° (3 mm) and 96-100° (3 mm). The three frequencies 1643, 1657, and 1672 cm^{-1} were found in the spectra of both these fractions, but the intensity of the last frequency was low in the first fraction. Taken in relation to the above discussion, this indicates that in this case fractionation through the column was not effective in completely removing the high-boiling isomer having a double-bond frequency of 1672 cm^{-1} from the first fraction.

The changes in the relative intensities of the double-bond frequencies in the tetramer fractions investigated confirm the conclusion that we reached on the basis of Raman data for triisobutene fractions, namely, that the pre-

* There is no basis for the first view; there is no frequency in the spectrum which could give an overtone at 1644 cm^{-1}. Neither does rotation isomerism occur; its absence is indicated by the great simplicity (small number of lines) of the spectrum of the low-boiling part of the trimer fraction after the double oxidation.

sence of several frequencies in the double-bond region is not the result of Fermi resonance and rotation isomerism, but is to be attributed to the presence of several isomers in which the double bond occupies various positions. When considered in relation to the above discussion, these changes indicate that by preferential oxidation of trisubstituted isomers and subsequent removal of oxidation products by distillation, the low-boiling tetramer fraction of isobutene can be caused to yield one of its major components, the isomer (XIV), in an almost pure state.

Double-bond Frequencies in Tetramer Fractions of Isobutene (Diisobutene Dimer) (cm^{-1})

Low-boiling fraction prepared over $ZnCl_2$ (diisobutene dimer):			
before oxidation	1640 (6*)	1656 (6*)	
after double oxidation	1643 (6*)	1659 (4*)	
Fractions obtained in presence of 3% sulfuric acid:			
b.p. 84-90° (3 mm)	1643 (5*)	1657 (6*)	1672 (2*)
b.p. 96-100° (3 mm)	1642 (5*)	1657 (5*)	1670 (5*)

It must be pointed out that the double-bond frequencies of the tetramer fractions, unlike those of the dimer and trimer fractions, are disposed on a strong general background, particularly in the case of the first two in the table (they are almost merged into one another). This may be the result of a larger number of tetramer isomers than of trimer, and still more, dimer isomers (of which there are only two). The double-bond frequencies of isomers present in small amounts may coincide with the cited tetramer frequencies, cause them to be diffuse, disappear against the general background, and to some extent be the source of this background.

The results of the investigation show that, in spite of Gross's results [15], in the lower fractions from the trimer onward there is a predominance of forms inactive in further polymerization; the active forms, by undergoing polymerization, pass into higher fractions. For the lower polymers, from the tetramer onward, there is not just one form [(IX), (X), etc.], as asserted in [15], but several.

SUMMARY

1. The available results of chemical and Raman spectrum investigations on the structure of isobutene polymers (trimers and tetramers) were found to be highly contradictory. In the present investigation chemical and Raman spectrum results are in agreement and indicate the predominance of the isomers (II), (V), (VI), and (XIV) in the appropriate fractions; from the trimer fraction onward these are inactive in further polymerization; the active forms [(VII), (IX), (X), etc] participate in the formation of higher polymers and do not accumulate in appreciable amount at the lower stages of polymerization.

2. The view that the doublet in the double-bond region of frequencies for lower polymers is the result of Fermi resonance and rotation isomerism is shown to be unsound. The doublet of frequencies arises from the presence of a mixture of isomers having different double-bond frequencies.

LITERATURE CITED

[1] A. M. Butlerov, J. Russ. Phys. Chem. Soc. 5, 187 and 302 (1873); 8, 279 and 351 (1876); 9, 38 (1877); 11, 197, (1879); 14, 199 (1882).

[2] E. E. Vagner, Oxidation of Unsaturated Hydrocarbons, Warsaw, 1888.*

[3] N. A. Prilezhaev, J. Russ. Phys. Chem. Soc. 39, 769 (1907).

[4] A. P. El'tekov, Reactions of Ethylene Hydrocarbons and Saturated Alcohols, Khar'kov Univ. Press, 1884.*

[5] S. V. Lebdev, Life and Works, ONTI, 1938.*

[6] F. Whitmore, K. Laughlin, J. Matuszevsky, J. Surmaits, J. Am. Chem. Soc. 63, 756 (1941); F. Whitmore, C. Wilson, J. Capinjola, C. Tonberg, G. Fleming, R. McGrew, J. Cosby, J. Am. Chem. Soc, 63, 2035 (1941; F. Whitmore, J. Surmaits, J. Am. Chem. Soc. 63, 2200 (1941).

[7] A. D. Petrov, Synthesis and Isomerizations of Hydrocarbons, Izd. AN SSSR, 1947.*

* In Russian.

[8] A. V. Topchiev, B. M. Tumerman, and V. N. Andronov, Trans. Gubkin Moscow Petroleum Inst., No. II, State Fuel Tech. Press, 1951, p. 185.

[9] A. P. Meshcheriakov, M. I. Batuev, and A. D. Petrov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1950, 282.

[10] D. Rauk, E. Bordner, J. Chem. Phys. 3, 248 (1935).

[11] Catalog of Selected Raman Spectral Data. Am. Petrol. Inst. Research, Project 44, Nat. Bur. Stand., Washington, 1948.

[12] F. Whitmore, Ind. Eng. Chem. 26, 94 (1934); F. Whitmore, C. Church, J. Am. Chem. Soc. 54, 3711 (1932).

[13] P. Bartlett, G. Fraser and R. Woodward, J. Am. Chem. Soc. 63, 495 (1941).

[14] A. D. Petrov, E. I. Erzuitova, and M. I. Batuev, Proc. Acad. Sci. USSR 64, 349 (1949).

[15] E. F. Gross, K. V. Nel'son, and Ia. M. Slobodin, Proc. Acad. Sci. USSR 75, 697 (1950); J. Phys. Chem. 25, 504 (1951); Ia. M. Slobodin and E. M. Markova, J. Gen. Chem. 22, 102 (1952).*

[16] N. A. Prilezhaev, Organic Petroxides and their Use in the Oxidation of Unsaturated Compounds, Warsaw, 1912.**

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SYNTHESIS OF POLYALKYLENEARYLS

COMMUNICATION 2. POLYCONDENSATION OF 1,2-DICHLOROETHANE WITH DIARYLALKANES

G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova

We have shown previously [1] that reaction between 1,2-dichloroethane and benzene in presence of aluminum chloride gives not only macromolecular polycondensation products, but also bibenzyl and p-diphenethylbenzene, which are evidently the primary low-molecular-weight products of this reaction. In order to provide proof of this view we studied the polycondensation of 1,2-dichloroethane with bibenzyl in presence of aluminum chloride. If our views are correct, then as in the polycondensation of dichloroethane with benzene, the product should be polyethylenephenyl. The experimental procedure was that used previously [1], with the exception that all the reactants were mixed in the cold in the reaction flask and were then heated with stirring. The results of two series of experiments are given in Tables 1 and 2.

TABLE 1

Polycondensation of 1,2-Dichloroethane with Bibenzyl
(bibenzyl : dichloroethane = 1.17 : 1; aluminum chloride 2.98 moles % on the amount of bibenzyl)

Temperature (°C)		Duration of experiment (minutes)	Yield of polyethylenephenyl (%)		Molecular weight of soluble polyethylenephenyl
at start of experiment	at end of experiment		soluble	cross-linked	
50	50	90	Reaction did not go		
60	95	90	78.5	1.1	21,900
70	95	90	78.5	1.7	18,000
90	100	63	84.1	Traces	19,000

The destructive oxidation of the polycondensation product from bibenzyl and 1,2-dichloroethane gave terephthalic acid, from which we may conclude that the product of the polycondensation of bibenzyl with 1,2-dichloroethane in presence of aluminum chloride is polyethylenephenyl. Hence, the bibenzyl formed in the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is not a by-product, but is an intermediate reaction product which takes part in the formation of polyethylenephenyl.

Reaction between bibenzyl and 1,2-dichloroethane can be represented as follows:

$$(n+1)\,C_6H_5CH_2CH_2C_6H_5 + n\,ClCH_2CH_2Cl \xrightarrow{AlCl_3} H(C_6H_4CH_2CH_2)_{2n+1}C_6H_5 + 2n\,HCl$$

In calculating the yield of polyethylenephenyl we assumed that one dichloroethane molecule gives the repeating unit $C_6H_4(CH_2)_2C_6H_4(CH_2)_2$.

It will be seen from Tables 1 and 2 that the results of the polycondensation of bibenzyl with 1,2-dichloroethane in presence of aluminum chloride depend not only on the catalyst concentration (for given relative amounts of reactants), but also on the temperature schedule and the duration of reaction. At low temperatures there is no

polycondensation; rise in temperature causes polycondensation to occur with formation of polyethylenephenyl of high molecular weight in good yield. However, in order to obtain soluble polymer which does not contain any appreciable amount of cross-linked polyethylenephenyl, rise in temperature must be accompanied by reduction in the duration of reaction; otherwise, much three-dimensional polymer is formed.

TABLE 2

Polycondensation of 1,2-Dichloroethane with Bibenzyl
(bibenzyl : dichloroethane = 1.17 : 1; temperature at start of experiment 85°; temperature at end 100°; duration of experiment 45 minutes)

Concentration of catalyst (moles % on bibenzyl)	Yield of polyethylenephenyl (%)		Molecular weight of soluble polyethylenephenyl
	soluble	cross-linked	
2.98	78.5	1.7	22,000
3.73	89.2	0.6	25,100
4.48	60.6	28.0	6,810

When the temperature schedule, duration of reaction, and relative amounts of reactants are maintained constant, the yield and molecular weight of soluble polyethylenephenyl depends on catalyst concentration.

As will be seen from Table 2, increase in the concentration of aluminum chloride to 3.73 moles percent (on the amount of bibenzyl) results in increase in the yield and molecular weight of the polyethylenephenyl. Further rise in catalyst concentration results in reduction in the yield of soluble polyethylenephenyl and a sharp fall in its molecular weight, and there is a great increase in the yield of insoluble, cross-linked polyethylenephenyl. The reduction in the molecular weight of the soluble polyethylenephenyl during the formation of three-dimensional polycondensation products is due to the preferential cross-linking of the longer molecules, as shown previously by two of us in collaboration with Soboleva [2].

The polycondensation of 1,2-dichloroethane with bibenzyl gives a polyethylenephenyl having a much higher molecular weight than the polyethylenephenyl obtained by the polycondensation of 1,2-dichloroethane with benzene [1]. This may be explained on the hypothesis that in the polycondensation of dichloroethane with bibenzyl the degradation reaction plays a less important part than in the polycondensation of dichloroethane with benzene; bibenzyl would appear to be a more feeble degrading agent than benzene. The feebleness of the degrading action of bibenzyl is indicated by the formation of polyethylenephenyl by the action of aluminum chloride on bibenzyl [3], since otherwise the transarylation of bibenzyl would be arrested at a low degree of polymerization.

1,2-Dichloroethane polycondenses not only with bibenzyl, but also with biphenyl, and the molecular weight of the product is higher when equimolecular amounts of reactants are used (5120) than when there is a 49 mole % excess of biphenyl (in both cases the aluminum chloride concentration was 10.0 moles % on the biphenyl). On the other hand, with equimolecular proportions of reactants and 9.0 mole % of aluminum chloride, 1,2-dichloroethane does not polycondense with diphenylmethane. This may be explained on the hypothesis that in the case of diphenylmethane the activating effect of the methylene group is distributed over two benzene nuclei so that the reactivities of hydrogen atoms in these nuclei are less than those in bibenzyl, in which the activating effect of a methylene group is distributed over one benzene nucleus. In biphenyl the activating group is phenyl; in diphenylmethane and bibenzyl the mutual effect of the phenyl groups is weakened by their greater distance apart and the presence of aliphatic bridges between the nuclei.

SUMMARY

A study was made of the polycondensation of 1,2-dichloroethane with bibenzyl. It was shown that 1,2-dichloroethane polycondenses with biphenyl, but not with diphenylmethane.

LITERATURE CITED

[1] G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 596.

[2] V. V. Korshak, G. S. Kolesnikov, and T. A. Soboleva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 365.*

[3] V. V. Korshak and G. S. Kolesnikov, Proc. Acad. Sci. USSR. 70, 625 (1950).

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HETEROCHAIN POLYESTERS

COMMUNICATION 6. MIXED ETHYLENE GLYCOL POLYESTERS OF TWO DICARBOXYLIC ACIDS

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A mixed polyester was first prepared by Carothers and Dorough [1] by the copolycondensation of ethylene glycol with succinic and sebacic acids. This mixed polyester differed in properties from the mixture obtained by melting polyethylene succinate and polyethylene sebacate together. Batzer [2] studied mixed polyesters obtained by the copolycondensation of 1,6-hexanediol with 2,9-dibutylsebacic and sebacic acids.

More attention has been given to the study of mixed aromatic-aliphatic polyesters. Edgar [3] prepared mixed polyesters of ethylene glycol with terephthalic and adipic acids and with terephthalic and sebacic acids taken in various proportions, and he studied the changes in melting point. Edgar [4] studied also the changes in the second-order transition temperature for mixed polyesters of ethylene glycol with terephthalic acid and various aliphatic dicarboxylic acids (as the second acid). Izard [5] gives the melting points of mixed ethylene glycol polyesters of terephthalic and sebacic acids taken in various proportions, and also of mixed ethylene glycol polyesters of sebacic and p,p'-(ethylenedioxy)dibenzoic acids. Griehl [6] studied the possibility of modifying polyethylene terephthalate and of using mixed terephthalic polyesters, particularly mixed terephthalic-sebacic polyesters, for the production of polyester fiber.

In the present investigation we prepared mixed polyesters by the polycondensation of bifunctional compounds. For this purpose we used various methods differing in the nature of the starting materials.

As starting materials we used bis-2-hydroxyethyl esters of dicarboxylic acids. In this case the monomeric esters were prepared separately and purified, and esterification was accelerated by the use of acid catalysts. However, in the case of many aliphatic acids the bis-2-hydroxyethyl esters were found to be very readily soluble, low-melting, or liquid substances. In vacuum distillation they were largely converted into polyesters and were therefore difficult to purify. In the esterification of dicarboxylic acids with ethylene glycol the formation of monomeric ester was accompanied by the formation of dimer and other polyesters of low molecular weight, which were difficult to remove. Uncertainty in the homogeneity of the original esters limited the applicability of this variant.

Mixed polyesters were prepared also by the transesterification of dimethyl esters of dicarboxylic acids with ethylene glycol. This method has an obvious advantage over the first, for the stability of the dimethyl esters ensures preservation of the proportions of the components, transesterification in presence of catalysts proceeds satisfactorily, and the dimethyl esters are readily purified by distillation or crystallization. Finally, mixed polyesters were prepared from two different straight polyesters, which were prepared beforehand. This method is interesting in that it completely removes the possibility of losing volatile components and altering the proportions of the reactants, since no volatile components are present in the straight polyesters.

In the present investigation we studied binary mixed polyesters of ethylene glycol with terephthalic acid and an aliphatic acid. Six binary systems were investigated: 1) terephthalic-oxalic; 2) terephthalic-succinic; 3) terephthalic-glutaric; 4) terephthalic-adipic; 5) terephthalic-azelaic; and 6) terephthalic-sebacic.

The results are given in Tables 1-8 and Figures 1-6.

TABLE 1

Terephthalic-Oxalic System

No.	Proportions (moles %)			Appearance			Temp. (°C)		Viscosity	Solubility***			
										ethanol		benzene	
	DME* – TA**	DME of oxalic acid	Ethylene glycol	Color	Transparency****	Consistency at room temp.	Softening	thread formation		at room temp.	at b.p.	at room temp.	at b.p.
1	0	100	300	Dark yellow	op	Brittle solid	146	148					
2	10	90	300	Yellow	op	»	75	87	0.28	–	–	+	+
3	30	70	300	White	op	»	158	172	0.13	–	–	–	–
4	50	50	300	»	op	»	203	218	0.15	–	–	–	–
5	70	30	300	»	op	»	229	238	0.21	–	–	–	–
6	90	10	300	»	op	»	234	246	0.19	–	–	–	–
7	100	0	300	»	op	Elastic solid	260	265	0.27	–	–	–	–

* DME - dimethyl ester.

** TA - terephthalic acid.

*** – denotes insolubility, + solubility, and O swelling.

**** op - opaque.

TABLE 2

Terephthalic-Succinic System

No.	Proportions (moles %)			Appearance			Temp. (°C)		Viscosity	Solubility					
										ethanol		ethyl acetate		cyclo-hexanone	
	BHE* – TA	Succinic acid	Ethylene glycol	Color	Transparency**	Consistency at room temp.	Softening	Thread formation		room temp.	at b.p.	room temp.	at b.p.	room temp.	at b.p.
1	0	100	200	Dark brown	op	Brittle solid	80	83	0.16	–	–	+	+	+	+
2	10	90	180	Same	op	Same	35	68	0.14	–	O	+	+	+	+
3	20	80	160	Dark red	tr	Viscous liquid	6	26	0.17	–	O	+	+	+	+
4	30	70	140	Same	tr	Rubbery	10	35	0.25	–	O	+	+	+	+
5	40	60	120	Light yellow	tr	Same	20	37	0.10	–	O	+	+	+	+
6	50	50	100	Same	tr	»	24	38	0.11	–	–	–	–	–	O +
7	60	40	80	Yellow	op	»	39	56	0.11	–	–	–	–	–	
8	70	30	60	Light yellow	op	Brittle solid	106	128	0.14	–	–	–	–	–	–
9	80	20	40	Same	op	»	180	202	0.15	–	–	–	–	–	–
10	90	10	20	White	op	»	216	224	0.13	–	–	–	–	–	–
11	100	0	0	»	op	Elastic solid	260	265	0.27	–	–	–	–	–	–

* BHE - bis-2-hydroxyethyl ester.

** tr - transparent.

TABLE 3

Terephthalic-Glutaric System

No.	Proportions (moles %)			Appearance			Temp. (°C)		Viscosity	Solubility			
										ethanol		benzene	
	DME–TA	DME of glutaric acid	Ethylene glycol	Color	Transparency*	Consistency at room temperature	Softening	Thread formation		at room temp.	at b.p.	at room temp.	at b.p.
1	0	100	300	Dark yellow	s/t	Viscous liquid	—23	—14	0.13	—	—	+	+
2	10	90	300	Same	s/t	Same	—26	—18	0.22	—	—	+	+
3	30	70	300	»	s/t	»	—6	14	0.11	—	—	+	+
4	50	50	300	White	op	Rubbery	100	109	0.22	—	—	—	+
5	70	30	300	»	op	Elastic solid	137	158	0.14	—	—	—	—
6	90	10	300	»	op	Same	210	223	0.28	—	—	—	—
7	100	0	300	»	op	»	260	265	0.27	—	—	—	—

* s/t - semitransparent.

TABLE 4

Terephthalic-Adipic System

No.	Proportions (moles %)			Appearance			Temp. (°C)		Viscosity	Solubility					
										ethanol		ethyl acetate		cyclohexanone	
	BHE – TA	Adipic acid	Ethylene glycol	Color	Transparency	Consistency at room temp.	Softening	Thread formation		room temp.	at b.p.	room temp.	at b.p.	room temp.	at b.p
1	0	100	200	Yellow	op	Brittle solid	35	38	0.12	—	—	+	+	+	+
2	10	90	180	Dark yellow	op	Same	32	35	0.12	—	—	+	+	+	+
3	20	80	160	Same	tr	Viscous liquid	—18	—8	0.10	—	—	+	+	+	+
4	30	70	140	»	tr	Same	7	16	0.14	—	—	+	+	+	+
5	40	60	120	Yellow	op	Brittle solid	45	61	0.12	—	—	—	+	+	+
6	50	50	100	»	op	Rubbery	103	127	0.15	—	—	—	+	+	+
7	60	40	80	Dark yellow	op	Elastic solid	165	172	0.20	—	—	—	—	—	+
8	70	30	60	Light yellow	op	Same	192	203	0.21	—	—	—	—	—	—
9	80	20	40	White	op	»	202	212	0.25	—	—	—	—	—	—
10	90	10	20	Light yellow	op	»	218	227	0.17	—	—	—	—	—	—
11	100	0	0	White	op	»	260	265	0.27	—	—	—	—	—	—

TABLE 5

Terephthalic-Azelaic System

No.	Proportions (moles %)			Appearance			Temp. (°C)		Viscosity	Solubility					
	BHE – TA	Azelaic acid	Ethylene glycol	Color	Transparency	Consistency at room temp.	Softening	Thread formation		ethanol		ethyl acetate		cyclohexanone	
										room temp.	at b.p.	room temp.	at b.p.	room temp.	at b.p.
1	0	100	200	White	op	Rubbery	45	47	0.49	–	–	–	+	–	+
2	10	90	180	Yellow	s/t	Same	35	40	0.70	–	–	+	+	+	+
3	20	80	160	»	tr	Viscous liquid	25	30	0.44	–	–	+	+	+	+
4	30	70	140	Light yellow	tr	Same	15	20	0.26	–	–	+	+	+	+
5	40	60	120	White	op	Rubbery	65	70	0.20	–	–	+	+	+	+
6	50	50	100	»	op	Same	96	110	0.21	–	–	–	+	+	+
7	60	40	80	»	op	Elastic solid	120	135	0.17	–	–	–	–	–	+
8	70	30	60	»	op	Same	136	141	0.15	–	–	–	–	–	–
9	80	20	40	»	op	»	195	198	0.13	–	–	–	–	–	–
10	90	10	20	»	op	»	225	227	0.14	–	–	–	–	–	–
11	100	0	0	»	op	»	260	265	0.27	–	–	–	–	–	–

TABLE 6

Terephthalic-Sebacic System

No.	Proportions (moles %)			Appearance			Temp. (°C)		Viscosity	Solubility					
	DME – TA	DME of sebacic acid	Ethylene glycol	Color	Transparency	Consistency at room temperature	Softening	Thread formation		ethanol		cyclohexanone		benzene	
										room temp.	at b.p.	room temp.	at b.p	room temp.	at b.p.
1	0	100	300	White	op	Elastic solid	70	73	0.25	–	–	+	+	+	+
2	10	90	300	»	op	Same	60	64	0.99	–	O	+	+	+	+
3	20	80	300	»	op	»	45	50	0.54	–	–	+	+	+	+
4	30	70	300	»	op	Rubbery	37	41	0.62	–	–	+	+	+	+
5	40	60	300	»	op	Same	60	75	0.55	–	–	+	+	+	+
6	50	50	300	»	op	»	115	125	0.40	–	–	–	+	–	+
7	60	40	300	»	op	»	127	132	0.21	–	–	–	+	–	+
8	70	30	300	»	op	Elastic solid	163	173	0.38	–	–	–	–	–	–
9	80	20	300	»	op	Same	190	195	0.60	–	–	–	–	–	–
10	90	10	300	»	op	»	198	212	0.55	–	–	–	–	–	–
11	100	0	300	»	op	»	260	265	0.27	–	–	–	–	–	–

TABLE 7

Relation of Melting Points (Temperatures of Thread Formation) (°C) of Various Mixed Polyesters to Proportions of Acids.

No.	Composition	Proportions of acids (moles %)									
		90 : 10	80 : 20	70 : 30	60 : 40	50 : 50	40 : 60	30 : 70	20 : 80	10 : 90	0 : 100
	Ethylene glycol										
1	Terephthalic-oxalic	246	–	238	–	218	–	172	–	87	148
2	Terephthalic-succinic	224	202	128	56	38	37	35	26	68	83
3	Terephthalic-glutaric	223	–	158	–	109	–	14	–	-18	-14
4	Terephthalic-adipic	227	212	203	172	127	61	16	-8	35	38
5	Terephthalic-azelaic	227	198	141	135	110	70	20	30	40	47
6	Terephthalic-sebacic	237	215	173	132	125	75	41	50	64	73

TABLE 8

Relation of Solubilities of Various Mixed Polyesters to Proportions of Acids*

(Solvent: cyclohexanone or benzene)

No.	Composition	Proportions of acids (moles %)									
		90 : 10	80 : 20	70 : 30	60 : 40	50 : 50	40 : 60	30 : 70	20 : 80	10 : 90	0 : 100
	Ethylene glycol										
1	Terephthalic-oxalic	–		–		–		–		+	–
2	Terephthalic-succinic	–	–	–	–	+	+	+	+	+	+
3	Terephthalic-glutaric	–		–		+		+		+	+
4	Terephthalic-adipic	–	–	–	+	+	+	+	+	+	+
5	Terephthalic-azelaic	–	–	–	+	+	+	+	+	+	+
6	Terephthalic-sebacic	–	–	–	+	+	+	+	+	+	+

* + indicates that the polyester is soluble, and – indicates that it is insoluble.

DISCUSSION OF RESULTS

The properties of the mixed polyesters under consideration in this paper depend greatly on the nature of the components and their proportions. Many of these polyesters are elastic solids; some of them are brittle solids. Some of them, particularly those prepared from equimolecular amounts of terephthalic and aliphatic acids, are highly elastic rubbery products. Others are soft waxy substances or highly viscous liquids.

Examination of Figures 1-6 shows that in all systems there are polyesters of minimum melting point having proportions of terephthalic and aliphatic acids of 10 : 90, 20 : 80, or 30 : 70 moles %. When we examine the change in melting point from one system to another for given proportions of terephthalic acid and the second acid, it is seen that at ratios of 90 : 10 and 80 : 20 the melting points are very close and the nature of the second acid has scarcely any effect. For the other ratios (70 moles % of terephthalic acid and less) the melting point varies from one system to another, i.e. is dependent on the nature of the second acid.

It should be noted that the minimum temperatures (Table 7) for the different systems follow a pattern similar to that found in each system. The minimum temperatures fall from 87° to -18° and then rise again to 41°. The melting point is dependent on the number of carbon atoms between the ester groupings in the polyesters.

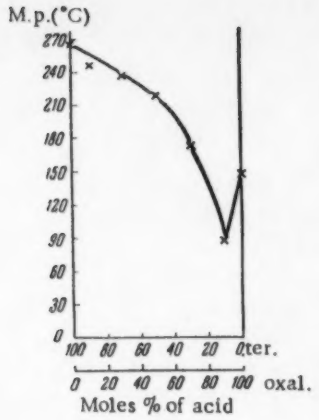

Fig. 1. Terephthalic-oxalic acids with ethylene glycol.

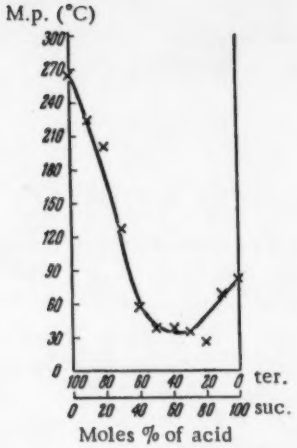

Fig. 2. Terephthalic-succinic acids with ethylene glycol.

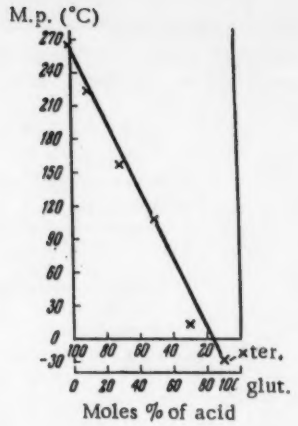

Fig. 3. Terephthalic-glutaric acids with ethylene glycol.

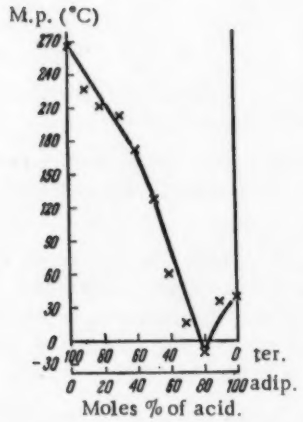

Fig. 4. Terephthalic-adipic acids with ethylene glycol.

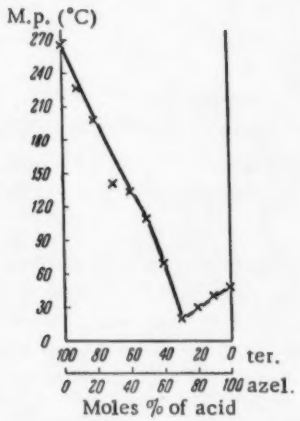

Fig. 5. Terephthalic-azelaic acids with ethylene glycol.

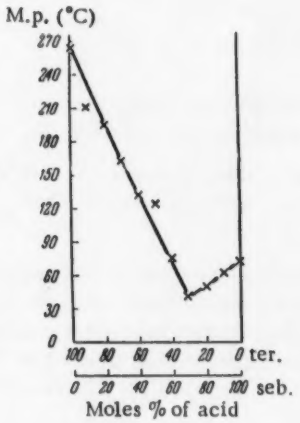

Fig. 6. Terephthalic-sebacic acids with ethylene glycol.

The solubility of the mixed polyesters in solvents such as benzene and cyclohexanone (Table 8) is determined by the terephthalic acid content. When more than 50-60 % of the acid component is terephthalic acid the polyester is insoluble; otherwise it is soluble in these solvents.

The properties of mixed polyesters depend on the relative amounts of the components. It was therefore of interest to determine the extent to which the relative amounts are preserved during reaction. Elementary analysis was carried out on terephthalic-sebacic polyesters prepared from different relative amounts of the acids. The results are given in Table 9. The results show that the calculated composition is fairly close to the composition found experimentally, which indicates preservation of the proportions of components.

EXPERIMENTAL

Polycondensation Procedure. The mixed polyesters were prepared in the apparatus described previously [7]. So that polycondensation with different proportions of components could be carried out under conditions as nearly alike as possible, reactions were carried out simultaneously in six test tubes in one bath. Polycondensation was carried out in two stages: the first stage, at lower temperatures, was carried out in a stream of nitrogen, and the

second, at higher temperatures, in a vacuum. Polycondensation in a stream of nitrogen was at 100-220° for 15-17 hours, and polycondensation in a vacuum was at 100-260° (with gradual rise of temperature) for 25-48 hours. The total duration of reaction was 40-65 hours.

TABLE 9

Carbon and Hydrogen Contents of Terephthalic-Sebacic Polyesters

Molar ratio of acids	Carbon (%)		Hydrogen (%)	
Terephthalic : sebacic	Found	Calculated	Found	Calculated
0 : 100	62.98; 62.84	63.16	8.95; 8.83	8.77
10 : 90	63.03; 62.95	63.10	8.12; 8.10	8.38
20 : 80	63.29; 63.46	63.04	7.71; 7.52	7.97
30 : 70	62.79; 62.74	62.98	7.51; 7.43	7.55
40 : 60	63.21; 63.26	62.92	7.15; 7.20	7.12
50 : 50	62.87; 62.60	62.86	6.68; 6.62	6.67
60 : 40	62.43; 62.41	62.79	6.18; 6.14	6.20
70 : 30	62.37; 62.30	62.73	5.65; 5.72	5.72
80 : 20	62.74; 62.50	62.65	5.21; 5.26	5.22
90 : 10	62.18; 62.28	62.58	4.83; 5.01	4.70
100 : 0	62.14; 61.98	62.50	4.20; 4.25	4.16

In order to characterize the mixed polyesters obtained, the following properties are listed in the tables: 1) appearance; 2) melting point; 3) viscosity of a 0.5 % solution in cresol; and 4) solubility.

Mixed polyesters do not have sharp melting points and pass from solid to liquid through the stage of softening. The start of the transition was taken as the softening point, and its final stage as the temperature of thread formation.

In the case of polyesters that are viscous liquids at room temperature, the melting point was determined as follows. The substance (0.1-0.2 g) was placed in a test tube and cooled in a cooling mixture until solid. The solid was then warmed slowly to room temperature: the softening point was taken to be the temperature at which the substance began to deform under the weight of the thermometer, and the temperature of thread formation was taken to be that at which the substance stuck to the thermometer and could be drawn into a thread.

Melting points below 250° were determined in the same way with the exception that the samples were heated under a layer of molten paraffin in order to eliminate the effect of atmospheric oxygen. Melting points above 250° were determined in a sealed capillary, which was heated in a brass block.

The solubilities of the mixed polyesters were determined qualitatively in several solvents. The polyester sample (0.2 g) was placed in a small flask and covered with solvent (4 ml). For the determination of solubility at room temperature, the flask was shaken intermittently for 2-3 hours. If the polyester did not dissolve at room temperature, the mixture was refluxed for 2-3 hours at the boiling point of the solvent.

SUMMARY

1. A series of mixed polyesters formed by ethylene glycol with terephthalic acid and an aliphatic acid were prepared, the two acids being taken in various proportions. The following aliphatic acids were used: oxalic, succinic, glutaric, adipic, azelaic, and sebacic.

2. The relationships between the melting points of these polyesters and the relative amounts of aromatic and aliphatic acids were determined.

3. The relationships between the solubilities of these polyesters and the relative amounts of aromatic and aliphatic acids were determined.

LITERATURE CITED

[1] W. H. Carothers, G. L. Dorough, J. Am. Chem. Soc. 52, 711 (1930).

[2] H. Batzer and F. Wiloth, Makromol Chem. 8, 41 (1952).

[3] O. B. Edgar and E. Ellery, J. Chem. Soc. 1952, 2633.

[4] O. B. Edgar, J. Chem. Soc. 1952, 2638.

[5] E. F. Izard, J. Pol. Sci. 8, 503 (1952).

[6] W. Griehl and R. Hoffmeister, Faserforsch. u. Textiltechn. 11, 504 (1955).

[7] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 164.*

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BRIEF COMMUNICATIONS

SYNTHESIS OF SOME ORGANOSILICONPHOSPHORUS COMPOUNDS

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We recently proposed [1] a simple method of preparing hydrolyzable organosiliconphosphorus compounds by reaction of aliphatic compounds with PCl_3 and O_2 [2, 3]. There are references to similar work in American literature, but only in review articles [4-6] in which no experimental data are given.

We have described the reaction of PCl_3 and O_2 with chloroethylsilanes and with tetraethylsilane [1]. Continuing the study of this reaction, we have shown that increase in the size of the radical in the original chloroalkylsilane results in some increase in the yield of the silylalkylphosphonic dichloride, but even in the most favorable case (dichloromethylpropylsilane) the yield did not exceed 13 %. The main reaction was the oxidation of phosphorus trichloride to phosphoryl chloride, which however did not proceed in absence of the organic compound. For the reaction of trichloro(1-chloroethyl)- and trichloro(2-chloroethyl)-silanes with PCl_3 and O_2 it was found that the resulting chloroethylphosphonic dichlorides were extremely unstable, decomposing even when kept in sealed tubes. Silicon tetrachloride was found in the decomposition products. Owing to decomposition, these compounds could be isolated in yields of only 1-2 %. 2-Chloro-2-(triethylsilyl)ethylphosphonic dichloride, obtained from triethylvinylsilane as follows:

$$(C_2H_5)_3SiCH=CH_2 + 2PCl_3 + O_2 \rightarrow (C_2H_5)_3SiCHClCH_2P(=O)Cl_2 + POCl_3$$

was also unstable, and it decomposed partially when distilled or kept. When chlorotrimethylsilane, benzyltrichlorosilane, and trichlorophenethylsilane were treated with PCl_3 and O_2, the organosilicon compounds were recovered unchanged and phosphorus trichloride was largely converted into phosphoryl chloride. Attempts to bring about reaction between various alkylchlorosilanes and PBr_3 or $C_6H_5PCl_2$ were not successful: PBr_3 was recovered quantitatively, and $C_6H_5PCl_2$ was largely converted into $C_6H_5POCl_2$.

Hydrolysis of 3-(trichlorosilyl)propylphosphonic dichloride (I) and of 3-(dichloromethylsilyl)propylphosphonic dichloride (II) gave resins that were partially soluble in water. When a mixture of 20 moles % of (I) or (II) with 80 moles % of CH_3SiCl_3 was hydrolyzed, a water-insoluble resin was formed. None of the resins obtained would support combustion, even when introduced into the flame of a gas burner.

EXPERIMENTAL

Reaction of Trichloropropylsilane with Phosphorus Trichloride and Oxygen. A mixture of 177.5 g (1 mole) of $C_3H_7SiCl_3$ and 274 g (2 moles) of PCl_3 was prepared in a one-liter round-bottomed flask fitted with reflux condenser and tube for the passage of oxygen. Dry oxygen was passed into the mixture at the rate of 4 liters per hour. As the result of reaction the temperature of the mixture rose to 50-70°. When oxygen had been passed for two hours without further rise in temperature, the reaction was stopped. Unchanged reactants and $POCl_3$ were distilled off under somewhat reduced pressure and were then fractionated through a column: this gave 17.5 g of PCl_3, 144.5 g of $C_3H_7SiCl_3$, and 257.5 g of $POCl_3$. Vacuum distillation of the residue gave 24.2 g of 3-(trichlorosilyl)--propylphosphonic dichloride, the properties and yield of which are given in the table. The results of other ex-

TABLE

Original organosilicon compound	Product	Yield (%) on amount of alkylchlorosilane that reacted	Yield (%) on original amount of alkylchlorosilane	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Found (%) C	Found (%) H	Found (%) Cl	Found (%) Si + P	Calculated (%) C	Calculated (%) H	Calculated (%) Cl	Calculated (%) Si+P
$n\text{-}C_3H_7SiCl_3$	$Cl_2SiC_3H_6P(=O)Cl$	72.2	8.2	134—142 (4)	1.5003	1.5202	12.48 12.60	2.12 2.10	59.30 59.12	20.15 29.20	12.18	2.03	60.07	20.30
$n\text{-}C_3H_7Si(Cl)_2CH_2Cl$	$Cl_2Si(CH_3)C_3H_6P(=O)Cl$	68.7	12.8	137—145 (4)	1.4978	1.4118	17.32 17.08	2.13 3.18	50.92 50.80	21.64 21.73	17.45	3.27	51.03	21.82
$CH_3CHClSiCl_3$	$Cl_2SiC_2H_4ClP(=O)Cl$	24.5	1.8	135—140(4.5)	1.5068	1.6328	6.99 7.12	0.80 0.80	66.66 66.84	18.68 18.82	7.59	0.95	67.40	18.98
$ClCH_2CH_2SiCl_3$	$Cl_2SiC_2H_4ClP(=O)Cl$	28.3	2.1	141—146 (4)	1.5125	1.6812	7.04 7.08	0.92 0.86	67.10 67.00	18.74 18.88	7.59	0.95	67.40	18.98
$(C_2H_5)_2SiCH=CH_2$	$(C_2H_5)_2SiC_2H_4ClP(=O)Cl$	21	8	130—131 (5)	1.4948	1.1844	31.28 31.58	6.00 6.12	35.54 35.64	20.32 20.13	32.38	6.07	35.95	20.23

periments carried out under the same conditions with the same relative amounts of reactants are also given in the table.

Hydrolysis of $Cl_3SiC_3H_6POCl_2$ (I) and $Cl_2Si(CH_3)C_3H_6POCl_2$ (II). Compound (I) or (II) (20 g) was dropped slowly with vigorous stirring into 250 ml of distilled water. The precipitate formed partially redissolved. Water was then evaporated away, and the resin was dried at 150° for ten hours. When a mixture of 20 moles % of (I) or (II) with 80 moles % of CH_3SiCl_3 was hydrolyzed under the same conditions, a water-insoluble resin was obtained.

SUMMARY

1. Five silicon-substituted alkyl- and chloroalkyl-phosphonic dichlorides were prepared by reaction of phosphorus trichloride and oxygen with trichloropropylsilane, with trichloro(1-chloroethyl)silane, with trichloro(2-chloroethyl)silane, with dichloromethylpropylsilane, and with triethylvinylsilane.

2. Resins formed by hydrolysis of the compounds synthesized are of low flammability.

LITERATURE CITED

[1] E. A. Chernyshev and A. D. Petrov, Proc. Acad. Sci. USSR. 105, 282 (1955).

[2] J. O. Clyton and W. L. Jensen, J. Am. Chem. Soc. 70, 3880 (1948).

[3] L. Z. Soborovskii, Iu. M. Zinov'ev, and M. A. Englin, Proc. Acad. Sci. USSR, 67, 293 (1949); 73, 333 (1950).

[4] Anonime, Chem. Eng. News 32, 1324 (1954).

[5] I. R. Elliott, M. Prober, P. D. George, Rubber Plastics Age 37, 315 (1956).

[6] P. D. George, M. Prober and I. R. Elliott, Chem. Revs. 56, No. 6 (1956).

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SYNTHESIS OF 3-(2-THIENYL)ALANINE

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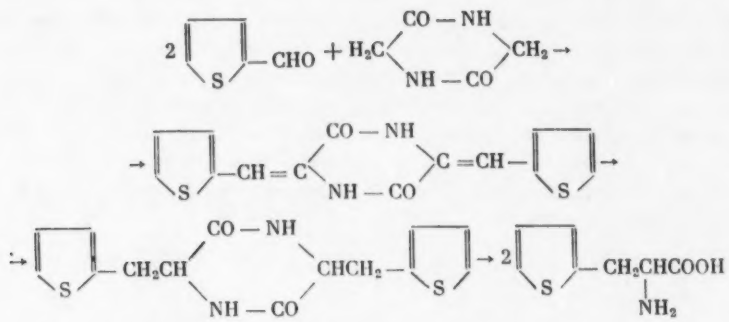
Recent results indicate that 3-(2-thienyl)alanine is biologically active in various different ways. Thus, being antagonistic to phenylalanine, it suppresses the development of certain microorganisms [1]; it also has an antivirus action [2] and is able to arrest the growth of malignant tumors [3]. In view of this interest in 3-(2-thienyl) alanine, investigations have been carried out on its synthesis. In 1950 Crowe and Nord [4] prepared this amino acid with the aid of the reaction of 2-thiophenecarboxaldehyde with rhodanine. According to their results, this method gives 3-(2-thienyl)alanine in good yield, so that it must be regarded as the most satisfactory of all methods known at present for the synthesis of this compound [5, 6]. However, in experiments on the synthesis of the analogous compound, 3-(2-furyl)alanine, the method based on the use of rhodanine [7] gave less satisfactory results than the synthesis from 2,5-piperazinedione, which was proposed by Sasaki [8]. This method gave 3-(2-furyl)alanine in very good yield, and we were prompted to investigate the possibility of synthesizing 3-(2-thienyl)alanine by Sasaki's method, ie. as follows:



Our experiments showed that the preparation of 3-(2-thienyl)alanine from 2,5-piperazinedione is comparatively simple and is more convenient than some of the methods described previously [5, 6], but it has no advantages over Crowe and Nord's method. The yield of 3-(2-thienyl)alanine obtained by the workers using rhodanine [4] (57 % on the thiophenecarboxaldehyde*) is higher than that which we obtained (36.5 % on the thiophenecarboxaldehyde, or 29 %, when recalculated on the thiophene taken).

EXPERIMENTAL

Condensation of Thiophenecarboxaldehyde with 2,5-Piperazinedione (Preparation of 3,6-Di-2-thenyldene--2,5-piperazinedione). A stirred mixture of 8.5 g (0.074 mole) of 2,5-piperazinedione, 20.8 g (0.186 mole) of thiophenecarboxaldehyde, 25 g of anhydrous sodium acetate, and 35 ml of acetic anhydride was heated for eight hours at a bath temperature of 126-130°. The solid mass obtained on cooling was treated several times with hot water, filtered off, carefully washed on the filter with hot water, and then boiled with a little alcohol. The residue, a light-brown powder, was filtered off, washed several times with ether, and dried in a vacuum desiccator.

* We calculated that the overall yield was 57 %, taking the single-stage yields given by the authors as our basis.

The product, amounting to 15.2 g, was a dark-yellow substance, m.p. 302-305° (with decomposition). After being recrystallized from acetic acid, 3,6-di-2-thenylidene-2,5-piperazinedione melted with decomposition at 310-314°.*

Found %: C 55.42; 55.58; H 3.30; 3.39; S 21.02; 20.88. $C_{14}H_{10}N_2O_2S_2$. Calculated %: C 55.59; H 3.33; S 21.20.

From the combined aqueous, alcoholic, and ethereal extracts, 3.1 g of unchanged 2-thiophenecarboxaldehyde was isolated. When calculated on the amount of thiophenecarboxaldehyde that reacted, the yield of unpurified 3,6-di-2-thenylidene-2,5-piperazinedione was 63.5 %.

Reduction of 3,6-Di-2-thenylidene-2,5-piperazinedione (Preparation of 3,6-Di-2-thenyl-2,5-piperazinedione). A suspension of 6.3 g (0.021 mole) of unpurified 3,6-di-2-thenylidene-2,5-piperazinedione in 600 ml of alcohol was shaken with 390 g of 3 % sodium amalgam, which was added in small portions with simultaneous neutralization of the reaction mixture with dilute (1 : 5) sulfuric acid. When reaction was complete (disappearance of the yellow precipitate and appreciable clearing of the solution), the precipitate was filtered off and the filtrate was evaporated to dryness under reduced pressure. This precipitate, which was a mixture of sodium sulfate and the reduction product, was treated with 200 ml of water; the undissolved part was filtered off, washed with water, and added to the residue from the evaporation of the alcoholic filtrate. The resulting 3,6-di-2-thenyl-2,5-piperazinedione was used, without prior purification, in the next stage of the process (hydrolysis). An analytically pure sample of 3,6-di-2-thenyl-2,5-piperazinedione, m.p. 263-265° with decomposition, was prepared by two crystallizations of the substance from alcohol in presence of activated charcoal.

Found %: C 54.73; 54.91; H 4.66; 4.75; S 20.72; 20.81. $C_{14}H_{14}N_2O_2S_2$. Calculated %: C 54.87; H 4.61; S 20.93.

Hydrolysis of 3,6-Di-2-thenyl-2,5-piperazinedione (Preparation of 2-(2-Thienyl)alanine). Unpurified 3,6-di-2-thenyl-2,5-piperazinedione prepared by the reduction of 6.3 g of 3,6-di-2-thenylidene-2,5-piperazinedione, was boiled for 24 hours with a solution of 48 g of crystalline barium hydroxide in 300 ml of water. After the addition of 300 ml of water, the solution was filtered and barium was precipitated with dilute sulfuric acid; barium sulfate was filtered off and washed several times with hot water. The filtrate was evaporated to dryness under reduced pressure; the residue, amounting to 5.3 g, was impure 3-(2-thienyl)alanine. A 3-g portion of the product was boiled with 60 ml of alcohol. The insoluble part was filtered off, washed with alcohol, and dissolved in 75 ml of water; the resulting solution was boiled with charcoal. The solution was cooled with ice, and crystals formed which were washed with ice water and dried in a vacuum desiccator over phosphoric oxide. The product, amounting to 1.5 g, was 3-(2-thienyl)alanine, m.p. 268° with decomposition (in a sealed capillary placed in an apparatus that had already been heated to 250°).

Found %: C 49.10; 49.30; H 5.46; 5.28; S 19.02; 18.94. $C_7H_9NO_2S$. Calculated %: C 49.10; H 5.30; S 18.73.

Alcohol (400 ml) and ether (150 ml) were added to the filtrate obtained after separation of the crystals. The solution was allowed to stand in a refrigerator, and a precipitate formed which was filtered off, washed with alcohol, and dried in a vacuum desiccator. The weight of this portion of 3-(2-thienyl)alanine was 0.8 g, m.p. 264° with decomposition. In admixture with 3-(2-thienyl)alanine synthesized by the method of Dittmer et al. [6] this substance showed no depression of melting point. For 3-(2-thienyl)alanine various authors [4-6] give melting points ranging from 246-246.5° to 273-275°. In all, 2.3 g of pure substance was obtained by the purification of 3.0 g of material. Thus, the overall yield of 3-(2-thienyl)alanine over the last two stages was 57 % on the 3,6-di-2-thenylidene-2,5-piperazinedione.

SUMMARY

3-(2-Thienyl)alanine was prepared by condensing 2-thiophenecarboxaldehyde with 2,5-piperazinedione, reducing the condensation product, and finally hydrolyzing the reduction product.

* The melting point of this substance was determined by heating it rapidly in a sealed capillary in a previously heated apparatus.

LITERATURE CITED

[1] M. F. Ferger, V. du Vigneaud, J. Biol. Chem. 174, 241 (1948); W. F. Drea, J. Bact. 56, 257 (1948); H. Pope, J. Bact. 58, 223 (1949); H. Kihara, and E. E. Snell, J. Biol. Chem. 212, 83 (1955).

[2] M. E. Rafelslon, H. A. Pearson and R. J. Winzler, Arch. Biochem. 29, 69 (1950); G. C. Brown, J. Immunol. 69, 441 (1952); H. R. Morgan, J. Exp. Med. 99, 451 (1954).

[3] J. A. Jacquez, C. C. Stock and R. K. Barclay, Cancer 6, 828 (1953); M. Rabinovitz, M. E. Olson, and D. M. Greenberg, J. Biol. Chem. 210, 837 (1954).

[4] B. F. Crowe, F. F. Nord, J. Org. Chem. 15, 81 (1950).

[5] Han-Ching Yuan, Hsueh-Chih Li. J. Chinese Chem. Soc. 5, 214 (1937); C. A. 33 496 (1938); G. Barger, A. P. T. Easson, J. Chem. Soc. 1938, 2100; J. V. Kostir, V. Kral, Collection Czechoslov. Chem. Communs 14, 263 (1949); N. F. Albertson, J. Am. Chem. Soc. 72, 1396 (1950).

[6] K. Dittmer, W. Herz, J. S. Chambers, J. Biol. Chem. 166, 541 (1946).

[7] C. Granacher, Helv. 5, 610 (1922).

[8] T. Sasaki, Ber. 54, 2056 (1921).

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ACTION OF TRIETHYLALUMINUM AND DIISOBUTYLALUMINUM HYDRIDE ON CHLORIDES OF GROUP VI METALS IN PRESENCE OF CARBON MONOXIDE. SYNTHESIS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN CARBONYLS

L. I. Zakharkin, V. V. Gavrilenko and O. Iu. Okhlobystin

The first investigation on the action of organometallic compounds on chlorides of Group VI metals in presence of carbon monoxide was that of Job and Cassal [1], who used organomagnesium compounds. They found that this reaction gave chromium, molybdenum, and tungsten carbonyls. This method of synthesizing carbonyls of Group VI metals with the aid of organomagnesium compounds was later studied in various forms by other investigators [2-4]. We have now shown that $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ can be prepared successfully by the use of triethylaluminum and diisobutylaluminum hydride.

In the reaction of chlorides of Group VI metals with triethylaluminum in ether solution at 120-130° in presence of carbon monoxide at 30-50 atm, we obtained $W(CO)_6$, $Mo(CO)_6$ and $Cr(CO)_6$ in yields of 86 %, 70 % and 54 %, respectively. In reaction under the same conditions with diisobutylaluminum hydride, $Cr(CO)_6$ and $Mo(CO)_6$ were obtained in yields of 73 % and 75 %, respectively. The preparation of triethylaluminum and of the triisobutylaluminum from which the diisobutylaluminum hydride was prepared was carried out by the reaction of Ziegler, Gellert, Zosel, and others [5] from aluminum, hydrogen, and the corresponding olefin.

As the procedure for this reaction is not described in detail in the literature, we shall describe the conditions that we used in the synthesis of $Al(C_2H_5)_3$ and $Al(i\text{-}C_4H_9)_3$.

EXPERIMENTAL

Preparation of Chromium Hexacarbonyl. a) A mixture of 15 g of anhydrous $CrCl_3$, 52 g of $Al(C_2H_5)_3$, and 100 ml of ether was prepared in a shaking autoclave. The initial pressure of carbon monoxide was 45 atm. The autoclave was heated at 120° for five hours. There remained 7 g of unchanged $CrCl_3$. The reaction mixture was poured onto ice, acidified with sulfuric acid, and steam-distilled. The crystals of chromium carbonyl were filtered off; some more of the carbonyl was obtained from the ethereal solution by removal of ether. The yield of $Cr(CO)_6$ was 6.1 g. b) A mixture of 9 g of $CrCl_3$, 58 g of $Al(i\text{-}C_4H_9)_2H$, and 100 ml of ether was prepared in a cooled autoclave. The initial pressure of carbon monoxide was 45 atm. The autoclave was left for one day at room temperature and was then heated for five hours at 130°. We recovered 1 g of unchanged $CrCl_3$. The usual treatment gave 8.1 g of $Cr(CO)_6$.

Found %: C 32.53; 32.52. C_6O_6Cr. Calculated %: C 32.74.

Preparation of Molybdenum Hexacarbonyl. a) A mixture of 15 g of $MoCl_5$, 31 g of $Al(C_2H_5)_3$, and 150 ml of ether was prepared in a cooled autoclave. The initial pressure of carbon monoxide was 40 atm. Reaction was for 90 minutes at room temperature and three hours at 120°. The usual method gave 10.2 g of $Mo(CO)_6$. b) A mixture of 13.7 g of $MoCl_5$, 45 g of $Al(i\text{-}C_4H_9)_2H$, and 150 ml of ether was prepared in a cooled autoclave; the initial pressure of carbon monoxide was 40 atm. Reaction was for four hours at 120°. The yield of $Mo(CO)_6$ was 10.1 g.

Found %: C 27.07; 17.01. C_6O_6Mo. Calculated %: C 27.28.

Preparation of Tungsten Hexacarbonyl. A mixture of 15.5 g of WCl_6, 28 g of $Al(C_2H_5)_3$, and 150 ml of ether was prepared in a cooled autoclave. The initial pressure of carbon monoxide was 42 atm. Reaction was for one

hour at room temperature and three hours at 120°. The yield of $W(CO)_6$ was 11.8 g.

Found %: C 20.62; 20.72. C_6O_6W. Calculated %: C 20.50.

Preparation of Triethylaluminum. The finely dispersed active aluminum required for the preparation of $Al(C_2H_5)_3$ and $Al(i\text{-}C_4H_9)_3$ was prepared by disintegration in a vibromill (3000 oscillations per minute at an amplitude of 3.5 mm) in 40-ml or 200-ml stainless steel vessels. Aluminum dust (average particle size 5-10 μ) (5-6 g) was placed in a hermetically sealed 40-ml vessel, which was three-quarters full of steel balls, 3.2 mm in diameter; 8-10 ml of a 5 % solution of triethylaluminum (or triisobutylaluminum) in heptane was added. After 7-12 hours of grinding we obtained an aluminum that was spontaneously inflammable in the air and had an average particle size of 1-2 μ. The balls were removed from the suspension of aluminum in heptane, and the suspension was used immediately for the reaction. A mixture of 60 g of active aluminum having an average particle size of 1-3 μ, 500 ml of heptane, and 160 g of triethylaluminum was prepared in a 2-liter rotating autoclave, and dry oxygen-free hydrogen was passed in (150-160 atm). The autoclave was heated to 110-115°, and a fall in pressure occurred which continued for two hours. When hydrogen ceased to be absorbed, the reaction mixture contained about 70% of diethylaluminum hydride and 30 % of triethylaluminum. When the reaction proceeds correctly no ethane is formed.* Excess of hydrogen was removed, and at room temperature dry oxygen-free ethylene was passed in (15-20 atm). The necessary amount of ethylene was absorbed in 20-30 minutes at 70-75°. The excess of ethylene was removed from the heated autoclave, and hydrogen was then passed and reaction was carried out as described above. After four repeats, reaction was complete. The solution was allowed to stand and then decanted from the precipitate. Removal of heptane under somewhat reduced pressure gave 327 g of triethylaluminum, b.p. 87-88° (3 mm).

Found %: Al 23. 80; 23.84. $C_6H_{15}Al$. Calculated %: Al 23.63.

In addition we obtained about 30 g of a higher-boiling fraction, b.p. 90-95° (3 mm), containing 20.4-20.8% of aluminum.

Preparation of Triisobutylaluminum. A mixture of 35 g of finely ground aluminum suspended in 200 ml of heptane, 20 g of triisobutylaluminum, and 600 ml of isobutene was prepared in a 2-liter rotating autoclave; the initial pressure of hydrogen was 150 atm. Reaction was complete in 90 minutes at 140°. Solvent was removed under reduced pressure. The yield of triisobutylaluminum, b.p. 55-56° (0.5 mm), was 210 g.

Found %: Al 13.81; 13.88. $C_{12}H_{27}Al$. Calculated %: Al 13.65.

In addition we obtained 40 g of a higher-boiling fraction (up to 100° at 0.5 mm) consisting mainly of diisobutylaluminum hydride. The reaction in which $Al(i\text{-}C_4H_9)_3$ is formed was accompanied by the side reaction of hydrogenation of isobutene, which may predominate when aluminum of high iron content is used (i.e. aluminum ground in iron vessels).

Preparation of Diisobutylaluminum Hydride. Triisobutylaluminum (31 g) was heated under reduced pressure at 150-160° for 1.5-2 hours. Isobutene condensed in a trap cooled with liquid nitrogen. The yield of diisobutylaluminum hydride, b.p. 95.5-96.5° (0.2 mm) and 116-118° (1 mm), was 20.5 g.

Found %: Al 18.82; 18.47; C 67.15; 67.17; H 13.18; 13.38. $C_8H_{19}Al$. Calculated %: Al 19.01; C 67.60; H 13.38.

SUMMARY

It was shown that reaction of carbon monoxide with chlorides of Group VI metals in presence of triethylaluminum or diisobutylaluminum hydride gives carbonyls of Group VI metals.

LITERATURE CITED

[1] A. Job and A. Cassal, C. r. 183, 392 (1926).

* When aluminum of average particle size 5-7 μ was taken, then there was no reaction below 120°. When the temperature was raised to 130-150°, another reaction set in, namely, hydrogenation of triethylaluminum:

$$(C_2H_5)_3Al + H_2 \rightarrow (C_2H_5)_2AlH + C_2H_6,$$

The yield of diethylaluminum hydride was almost quantitative.

[2] W. Hieber, and E. Romberg, Z. anorg. Chem. 221, 321 (1935).

[3] M. Windsor and Q. Blanchard, J. Am. Chem. Soc. 56, 823 (1934).

[4] B. B. Owen, J. English, H. G. Cassidy and C. V. Dundon, J. Am. Chem. Soc. 69, 1723 (1947).

[5] K. Ziegler, H. G. Gellert, K. Zosel, W. Lehmkuhl and W. Pfohl, Ang. Chem. 67, 424 (1955).

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HYDROGENATION OF CYCLOPROPYLBENZENE IN PRESENCE OF PALLADIUM AND PLATINUM BLACKS

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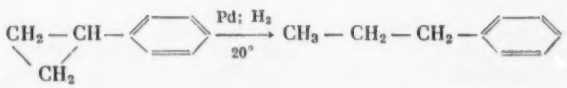
We have shown previously that systems in which a three-membered ring and a double bond (C = C or C = O) are conjugated together are readily hydrogenated in the cold with opening of the ring, particularly in presence of palladium black [1-4]. We now describe the hydrogenation of cyclopropylbenzene, in which a three-membered ring is conjugated with an aromatic system of double bonds. It was found that, in presence of palladium, hydrogen adds to cyclopropylbenzene at an average rate of 30 ml per minute and that hydrogenation ceases when one molecular proportion of hydrogen has been absorbed. The catalyzate boiled within a range of 0.1° and consisted, according to its constants, of pure propylbenzene:



Here, as in previously described cases, the three-membered ring opened at a bond of the substituted carbon; the benzene nucleus was not hydrogenated.

The hydrogenation of cyclopropylbenzene in presence of platinum black went quite differently. Even in presence of large amounts of catalyst, the rate of hydrogenation was only about one-ninetieth of the rate over palladium, and it diminished to such an extent in the course of time that we were unable to complete the reaction. In experiments with small amounts of hydrocarbon the amount of hydrogen absorbed attained 1.2-1.6 molecular equivalents; in the hydrogenation of a large amount of cyclopropylbenzene the experiment was discontinued after the absorption of one molecular equivalent of hydrogen because the rate of hydrogen fell to 2-3 ml per hour. Fractionation of the catalyzate from this experiment showed that it differed substantially from the catalyzate obtained by the addition of one molecule of hydrogen to cyclopropylbenzene in presence of palladium, for it was not a pure substance, but a mixture of hydrocarbons. The fractionation curve indicated that, apart from cyclopropylbenzene and propylbenzene, the catalyzate contained also propylcyclohexane and possibly cyclopropylcyclohexane, the constants of which have not been reported in the literature.

EXPERIMENTAL

Cyclopropylbenzene was prepared by the decomposition of the pyrazoline base obtained by the action of hydrazine hydrate on cinnamaldehyde [5]. After vacuum distillation through a column of about 30 theoretical plates the hydrocarbon had the following constants: b.p. 91.4-91.5° (52 mm); n_D^{20} 1.5337; d_4^{20} 0.9415. The constants reported in the literature for cyclopropylbenzene and its possible hydrogenation products are given in Table 1. The procedure for the hydrogenation and the isolation of the catalyzates has been described previously [1]. The catalyzates were distilled through a column of 30 theoretical plates.

1. Hydrogenation in presence of Palladium Black. Cyclopropylbenzene (16.9 g) was hydrogenated in 35 ml of alcohol in presence of 0.35 g of palladium black, and 3680 ml* of hydrogen was absorbed (one molecular proportion was 3463 ml). The average rate of hydrogenation was 1800 ml per hour. Fractionation of 16.5 g of cata-

* The volume of hydrogen was reduced to standard conditions.

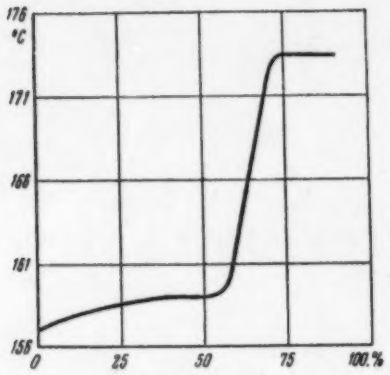


Fig. 1.

lyzate gave 15.2 g of a substance of b.p. 159.2-159.3° (760 mm), n_D^{20} 1.4920; d_4^{20} 0.8623. Residue 0.4 g, losses 0.9 g. The constants of the catalyzate indicated that it was propylbenzene.

2. Hydrogenation in presence of Platinum Black. Cyclopropylbenzene (10.6 g) was hydrogenated in 30 ml of alcohol in presence of 0.82 g of platinum black. The average rate of hydrogenation was 20 ml per hour. Hydrogenation was stopped after the absorption of one molecular proportion of hydrogen (2033 ml*). The amount taken for fractionation was 9.1 g. The fractionation results are given in Table 2 and Fig. 1. Consideration of the fractionation curve and of the data in Tables 1 and 2 shows that propylcyclohexane and propylbenzene may be present in Fractions I, II, and III; Fraction V is unchanged cyclopropylbenzene; and Fraction IV is an intermediate fraction.

TABLE 1

Hydrocarbon	B. p. (°C at 760 mm)	n_D^{20}	d_4^{20}
Cyclopropylbenzene [5]	173.6	n_D^{15} 1.5342	d_0^{20} 0.9401
Propylbenzene [6]	159.217	1.49202	0.86204
Isopropylbenzene [6]	152.392	1.49145	0.86179
Propylcyclohexane [6]	156.724	1.43705	0.79360
Isopropylcyclohexane [7]	154.56	1.4409	0.8022

TABLE 2

Fraction	B.p. (°C at 760 mm)	Weight (g)	Weight (%)	n_D^{20}	d_4^{20}
I	157.0—158.2	1.8	19.7	1.4730	0.8414
II	158.2—158.9	2.4	26.4	1.4830	0.8538
III	158.9—160.1	1.1	12.2	1.4890	0.8606
IV	160.1—173.3	2.0	21.9	1.5132	0.9049
V	173.3	0.5	9.9	1.5321	0.9418
	Residue	0.5			
	Losses	0.9			

SUMMARY

Substantial differences were found in the course of reaction in the hydrogenation of cyclopropylbenzene in the presence of platinum and palladium blacks.

LITERATURE CITED

[1] B. A. Kazanskii, M. Iu. Lukina, A. I. Malyshev, V. T. Aleksanian, and Kh. E. Sterin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 36.**

[2] B. A. Kazanskii, M. Iu. Lukina, A. I. Malyshev, V. T. Aleksanian, and Kh. E. Sterin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 1102.**

* The volume of hydrogen was reduced to standard conditions.

** Original Russian pagination. See C. B. Translation.

[3] B. A. Kazanskii, M. Iu. Lukina, and L. G. Sal'nikova, Proc. Acad. Sci. USSR 115, 301 (1957).*

[4] B. A. Kazanskii, M. Iu. Lukina, and L. G. Sal'nikova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1401.*

[5] N. M. Kizhner, J. Russ. Chem. Soc. 45, 949 (1913).

[6] F. D. Rossini and others, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh, 1953.

[7] A. F. Forziati, F. D. Rossini, J. Res, Natl. Bur. Stand. 43, 473 (1949).

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CATALYTIC REACTIONS AT THE SURFACE OF SOLID CALCIUM AND POTASSIUM AMIDES

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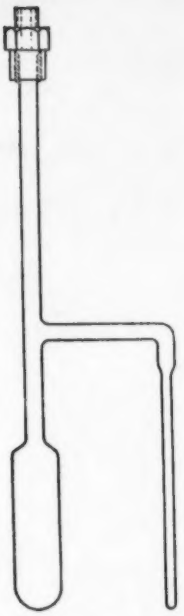
Amide ions in liquid deuterated ammonia catalyze isotopic exchange of hydrogen in hydrocarbons. The latter exhibit acidic properties and give up a proton to the amide ion, which has an extremely high affinity for protons [1]. In the study of deuterium exchange in alkenes in presence of potassium amide solution as catalyst, it was noted that isomerization occurs with displacement of the double bond [2, 3]. The isomerization is catalyzed also by solid calcium amide in absence of solvent [4, 5]. The isomerization of alkenes is one of the few examples of alkali-catalyzed reactions that proceed both under homogeneous and under heterogeneous conditions [6].

It has been suggested [5] that the isomerism proceeds through the stage of carbanion formation. There can be no doubt that isomerization reactions and deuterium-exchange reactions have the same origin and that these reactions are acid-base processes. It would be expected, therefore, that, in presence of a deuterated amide [it is immaterial whether it is $Ca(ND_2)_2$ or KND_2] containing adsorbed deuterated ammonia, isomerization of an alkene may be accompanied by replacement of hydrogen by deuterium. In view of the fact that in liquid deuterated ammonia, potassium amide catalyzes exchange reactions not only in alkenes, but also in other hydrocarbons, in particular aromatic hydrocarbons, we expected that isotopic exchange of hydrogen would be possible in the latter hydrocarbons when heterogeneous catalysis by solid deuterated amides is applied. In this preliminary communication we report results of experiments in which 2-methyl-1-butene or benzene was heated with solid $Ca(ND_2)_2$ or KND_2.

EXPERIMENTAL

Calcium amide was prepared as follows. A weighed amount of finely ground calcium was placed in a glass ampoule of the design shown in the figure. The ampoule was fixed by means of Wood's alloy into a steel component which could be screwed into a steel apparatus having a valve (see [7], Fig. 3). Liquid ND_3 was added. The formation of $Ca(ND_2)_2$ proceeded very slowly (one or two weeks), and in order to accelerate it ferric oxide was added (it catalyzes the conversion of calcium hexaammine into the amide). KND_2 was prepared by reaction between heavy ammonia and potassium. In order to obtain a uniform distribution of the amide on the surface of the ampoule, ammonia was driven off rapidly and the residual traces were pumped off while the ampoule was heated in a water bath. The necessary amount of pure hydrocarbon (distilled over sodium) was poured into a small ampoule, which was screwed into the second opening of the apparatus with a valve; the apparatus was turned upside down and by opening the valve the hydrocarbon was passed into the cooled evacuated ampoule containing the amide. The ampoule containing the reaction mixture was then resealed and placed in the thermostat. In order to distill off the hydrocarbon after the experiment, the capillary side arm of the ampoule was placed in liquid nitrogen, the capillary containing the substance was cut off, and the substance was distilled over calcined nickel sulfate in order to trap traces of ammonia, if present. After the experiment the refractive index of the hydrocarbon was determined. The hydrocarbon was burnt, the water formed was purified, and its density was determined by the drop method [8]. In all, sixty experiments were carried out. In the main series of experiments the amides were deuterated to the extent of 90 atoms percent. The relative amounts of amide and hydrocarbon were kept approximately constant: 1.1-1.2 g of $Ca(ND_2)_2$ or 0.5-0.6 g of KND_2 and 0.10-0.20 g of hydrocarbon, i.e. 5-12 molecules of Ca amide or 4-8 molecules of K amide per molecule of hydrocarbon. The temperature of the thermostat was 70°. We shall give the results of the main series of experiments.



2-Methyl-1-butene and $Ca(ND_2)_2$. Refractive index measurements on the reaction product showed that equilibrium was attained in the isomerization reaction after only 10-20 minutes; the refractive index of the hydrocarbon before the experiment was n_D^{20} 1.3778; and after the treatment with calcium amide it was n_D^{20} 1.385-1.388. Discrepancies were found in individual experiments. The deuterium-exchange results were as follows (the first figure is the duration of heating, and the second is the deuterium concentration in atoms %): 10 minutes - 0.3; 10 minutes - 0.2; 20 minutes - 0.1; 20 minutes - 0.5; 30 minutes - 2.5; 30 minutes - - 0.4; 1 hour - 0.9; 2 hours - 1.2; 4 hours - 2.0; 5 hours - 3.6; 6 hours - - 4.3; 6 hours - 1.2; 9 hours - 3.6; 9 hours - 11.3.

These results show that hydrogen exchange occurs between 2-methyl--1-butene and its isomers and solid calcium amide. The poor reproducibility of the results is probably to be explained mainly by variation in the surface area of amide from experiment to experiment. It is possible also that the amount of residual adsorbed ammonia on the amide varies.* Although the poor reproducibility makes quantitative comparisons difficult, it is clear that equilibrium is attained more rapidly in the isomerization reaction than in the exchange reaction.

2-Methyl-1-butene and KND_2: 20 minutes - 0.1; 7 hours - 1.3; 20 hours - 1.3; 27 hours - 3.6; 28 hours - 4.2. These measurements show that not only calcium amide, but also potassium amide brings about the exchange reaction.

Benzene and KND_2: 1 hour - 6.9; 1 hour - 5.8; 7 hours - 20; 7 hours - 7.9. In two experiments with calcium amide at 120° we succeeded in introducing more than 30 atoms percent of deuterium into benzene. The experiments with benzene show that the exchange reaction proceeds also with the nonisomerizing hydrocarbon benzene; moreover, it proceeds even more readily than with 2-methyl-1-butene.

Hence, not only the isomerization of alkenes, but also deuterium exchange in unsaturated and aromatic hydrocarbons is catalyzed by amide ions in ammoniacal solution and by solid amides under heterogeneous conditions. This confirms the view that the two reactions have the same origin, and it points also to a similarity in mechanism between reaction in solution and reaction at a solid surface. There are numerous data in the literature on the catalysis of reactions (including isomerization and deuterium exchange) by acids and by solid catalysts having acid properties (e.g. aluminum silicates, for which the acidity function H_0 has been measured [11]). On the other hand, there are scarcely any data on alkaline heterogeneous catalysis [6]. Hence, our observations, which to a certain extent fill this gap, are of interest for the theory of catalysis.

Alkaline heterogeneous catalysis of the isomerization of hydrocarbons and of isotopic exchange of hydrogen merits further investigation.

SUMMARY

It was shown that isomerization of alkenes with displacement of the double bond and hydrogen exchange in hydrocarbons both belong to the class of acid-base reactions; they are catalyzed by amide ions in ammoniacal solutions and by solid amides under heterogeneous conditions.

LITERATURE CITED

[1] A. I. Shatenshtein, Prog. Chem. 24, 377 (1955).

* We attempted to desorb ammonia as completely as possible and check whether the exchange reaction then occurred, but we met with difficulties. When calcium amide was heated in a vacuum, decomposition occurred (probably with formation of imide), and melted potassium amide reacts with glass [9]. In order to lower the melting point of the amide and facilitate the removal of ammonia, we decided to use a low-melting mixture of sodium and potassium amides [10], but its high viscosity made complete removal of ammonia difficult.

[2] A. I. Shatenshtein, L. N. Vasil'eva and N. M. Dykhno, Proc. Acad. Sci. USSR 85, 381 (1952); J. Phys. Chem. 28, 196 (1954).

[3] A. I. Shatenshtein and E. A. Izrailevich, Proc. Acad. Sci. USSR 108, 294 (1956).*

[4] I. V. Gostunskaia and B. A. Kazanskii, J. Gen. Chem. 25, 1995 (1955).*

[5] I. V. Gostunskaia, N. I. Tiun'kina, and B. A. Kazanskii, Proc. Acad. Sci. USSR 108, 473 (1956).*

[6] I. I. Ioffe and S. Z. Roginskii, J. Phys. Chem. 31, 612 (1957).

[7] A. I. Shatenshtein, J. Phys. Chem. 15, 246 (1941).

[8] A. I. Shatenshtein and Ia. M. Varshavskii, J. Anal. Chem. 11, 746 (1956).*

[9] P. V. Paterson and F. W. Bergstrom, Ind. Eng. Chem. 6, 136 (1934).

[10] C. A. Kraus and E. J. Cuy, J. Am. Chem. Soc. 45, 712 (1923).

[11] H. A. Benesi, J. Am. Chem. Soc. 78, 5490 (1956).

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SYNTHESIS OF KETO ACIDS FROM OLEFINS AND ω-CHLOROFORMYL CARBOXYLIC ESTERS

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Among existing methods [1-4] of preparing keto acids, catalytic methods deserve attention, particularly those based on the use of alkenes of known structure and of anhydrides and acid chlorides of mono- and di-basic acids. In the reaction of acid chlorides with alkenes in presence of metal halides the acid chlorides add at the double bond in such a way that the halogen goes to the least hydrogenated carbon atom and the acyl residue to the most hydrogenated atom [5]. In view of the fact that the anhydrides of the monoethyl esters of the acids that we have studied (oxalic, succinic, adipic) scarcely react at all with α-alkenes of normal structure, we used their more reactive acid chlorides for the synthesis of keto acids:

$$R-CH=CH_2 + ClC(=O)-(CH_2)_nCOOC_2H_5 \xrightarrow{ZnCl_2} R-CH(Cl)-CH_2-C(=O)-(CH_2)_nCOOC_2H_5$$

$$\xrightarrow[H_2]{10\%\ Pd(CaCO_3),\ 10\%\ KOH} R-CH_2-CH_2-C(=O)-(CH_2)_nCOOK \xrightarrow{10\%\ H_2SO_4}$$

$$R-CH_2-CH_2-C(=O)-(CH_2)_nCOOH.$$

EXPERIMENTAL

6-Oxo-7-decenoic Acid $C-C-C=C-C-C-C-C-C-COOH$ (with $=O$ on the second carbon); $C_{10}H_{16}O_3$. Reaction between 1-butene and ethyl 5-(chloroformyl)valerate [b.p. 155-158° (60 mm); d_4^{20} 1.089; n_D^{20} 1.4399] in presence of zinc chloride at 0° for two hours and at 20° for eight hours in a agitated metal flask (mechanical shaker) gave a 60% yield of ethyl 6-oxo-7-decenoate [b.p. 145-150° (6 mm); d_4^{20} 1.0098; n_D^{20} 1.4363]. Boiling of this for three hours with 10% alcoholic KOH gave the potassium salt of the keto acid, and treatment of this with 15 % sulfuric acid gave a 37.5 % yield of 6-oxo-7-decenoic acid, b.p. 165-175° (3 mm).

8-Methyl-6-oxo-7-nonenoic Acid $C-C(C)=C-C(=O)-C-C-C-C-COOH$; $C_{10}H_{16}O_3$. Reaction between isobutene and adipoyl chloride [b.p. 148-149° (5 mm)] in presence of zinc chloride at 0° with constant stirring gave the acid chloride of the keto acid. Treatment of this with 10 % KOH solution for four hours in a water bath gave the potassium salt of the keto acid, and by the action of 10 % sulfuric acid the keto acid $C_{10}H_{16}O_3$ was obtained in 15 % yield (m.p. 30-31°).

4-Oxodecanoic Acid $C-C-C-C-C-C-C(=O)-C-C-COOH$; $C_{10}H_{18}O_3$. Reaction of 1-hexene (b.p. 63.5-64.0°) with ethyl 3-(chloroformyl)propionate [b.p. 90-95° (10 mm)] in presence of zinc chloride at 20° for

ten hours with stirring in a Grignard apparatus gave ethyl 6-chloro-4-oxodecanoate in 45 % yield. After elimination of HCl and hydrogenation over a catalyst (10 % Pd on $CaCO_3$ [6]) at 20°, this gave 4-oxodecanoic acid, m.p. 60° (from 50 % ethanol), in 31 % yield.

6-Oxododecanoic Acid $C-C-C-C-C-C-\underset{\underset{O}{\|}}{C}-C-C-C-C-COOH$; $C_{12}H_{22}O_3$. Reaction of 1-

-hexene with ethyl 5-(chloroformyl)valerate in presence of zinc chloride under similar conditions gave ethyl 8--chloro-6-oxododecanoate in 44 % yield [b.p. 168-173° (30 mm)]. Hydrolysis and hydrogenation gave 6-oxododecanoic acid, m.p. 54-56°, in 26 % yield; its semicarbazone had m.p. 126°. We prepared this acid also by organomagnesium synthesis from hexylmagnesium bromide (b.p. 153-155°) and the anhydride of monoethyl adipate [b.p. 188-198° (2 mm)]; it had the same melting point. Mixture tests on the keto acids and the semicarbazones showed no depression.

7,7,8-Trimethyl-6-oxo-8-nonenoic Acid $C=\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{O}{\|}}{C}-C-C-C-C-COOH$; $C_{12}H_{20}O_3$. Reaction

of 2,3-dimethyl-2-butene (b.p. 72-73°; d_4^{20} 0.7028; n_D^{20} 1.4120), obtained by the dehydration of pinacolyl alcohol over $ZnCl_2$ on pumice at 180-220°, and ethyl 5-(chloroformyl)valerate in presence of $ZnCl_2$ gave ethyl 8-chloro--7,7,8-trimethyl-6-oxononanoate [b.p. 152-155° (8 mm); d_4 0.9822; n_D^{20} 1.4529] in 82.4 % yield. Boiling for two hours with 10 % alcoholic KOH and fractionation of the product gave 7,7,8-trimethyl-6-oxo-8-nonenoic acid [b.p. 175-180° (2 mm)] in 79 % yield.

7,7,8-Trimethyl-6-oxononanoic Acid $C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{O}{\|}}{C}-C-C-C-C-COOH$; $C_{12}H_{22}O_3$. Hydrogenation

of 7,7,8-trimethyl-6-oxo-8-nonenoic acid over a catalyst (10 % Pd on $CaCO_3$) at room temperature gave 7,7,8--trimethyl-6-oxononanoic acid [b.p. 193-195° (5 mm)] in 53 % yield.

6-Oxotridecanoic Acid $C-C-C-C-C-C-\underset{\underset{O}{\|}}{C}-C-C-C-C-C-COOH$; $C_{13}H_{24}O_3$. Reaction of

1-heptene (b.p. 93.0-93.5°; d_4^{20} 0.6949; n_D^{20} 1.4002) with ethyl 5-(chloroformyl)valerate in presence of zinc chloride gave ethyl 8-chloro-6-oxotridecanoate ($C_{13}H_{27}ClO_3$) in 72 % yield. Hydrolysis with simultaneous hydrogenation over a catalyst (10 % Pd on $CaCO_3$) gave 6-oxotridecanoic acid, m.p. 66-68°, in 50 % yield. Its semicarbazone had m.p. 124.5-125.0°.

SUMMARY

The following were synthesized for the first time by the catalytic method from the corresponding alkene and acid chloride: 1) 6-oxo-7-decenoic acid; 2) 8-methyl-6-oxo-7-nonenoic acid; 3) 4-oxodecanoic acid; 4) 6-oxododecanoic acid; 5) 7,7,8-trimethyl-6-oxo-8-nonenoic acid; 6) 7,7,8-trimethyl-6-oxononanoic acid; 7) 6-oxotridecanoic acid (this acid was prepared previously by organomagnesium synthesis [4]).

LITERATURE CITED

[1] J. Schreiber, C. r. Acad. Sci. 238, 1037 (1954).

[2] N. P. Buu-Hoi, Rec. trav. chim. 72, 84 (1953).

[3] R. P. Linstead, L. N. Owen, and R. F. Webb, J. Chem. Soc. 1218 (1953).

[4] J. Plesek, Collection Czech Chem. Commun. 21, No. 5, 1312 (1956).

[5] A. P. Meshcheriakov and L. V. Petrova, Proc. Acad. Sci. USSR 103, No. 2 (1955).

[6] B. R. Mozingo, Org. Syntheses 26, 77 (1946); Organic Syntheses (Russian translation). Collection 4, 1951, p. 341.

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SYNTHESIS OF DIVINYL TARTRATE

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The synthesis of vinyl ethers and esters by reaction of vinyl acetate with alcohols or acids has been described in the literature [1, 2]. By adjustment of the reaction temperature both vinyl ethers and esters may be synthesized by this method. The vinylation of acids with vinyl acetate can be represented as follows:

$$CH_2{=}CHOCOCH_3 + RCOOH \xrightarrow[HgSO_4]{20-80^\circ} CH_2 = CHOCOR + CH_3COOH.$$

By this method of "indirect vinylation" vinyl esters of the following mono- and di-basic acids have been prepared: stearic, lauric, benzoic, succinic, and adipic [2, 3].

Vinyl esters of monobasic hydroxy acids have been described in the literature [4]. We carried out experiments on the synthesis of the divinyl ester of a dibasic acid containing two hydroxy groups, i.e. D-tartaric acid. Divinyl tartrate was synthesized as follows:

$$HOOC-\underset{OH}{CH}-\underset{OH}{CH}COOH + 2CH_2 = CHOCOCH_3 \rightarrow$$

$$\rightarrow CH_2 = CHOOC-\underset{OH}{CH}-\underset{OH}{CH}-COOCH = CH_2 + 2CH_3COOH$$

This reaction was accompanied by the formation of ethylidene diacetate, which resulted from reaction between vinyl acetate and acetic acid:

$$CH_2 = CHOCOCH_3 + CH_3COOH \rightarrow CH_3CH\begin{matrix}OCOCH_3\\ \diagdown\\ \diagup\\ OCOCH_3\end{matrix}$$

Divinyl tartrate was found to be faintly colored viscous liquid, soluble in ether, acetone, benzene, and alcohol. It was quantitatively hydrolyzed in the cold when shaken with aqueous alkali. Divinyl tartrate polymerizes in presence of benzoyl peroxide or 2,2'-azobis[2-methylpropionitrile] and can be copolymerized with methyl methacrylate.

EXPERIMENTAL

A mixture of 75 g (0.5 mole) of tartaric acid, 520 g (6 moles) of vinyl acetate, 0.03 g of copper resinate, and 3 g of mercuric acetate was prepared in a one-liter three-necked flask fitted with stirrer, reflux condenser, and tube for the passage of nitrogen. The mixture was stirred vigorously while 0.75 g of 100 % sulfuric acid was added, and it was then heated to 80° in a water bath. Heating with stirring was continued until the precipitate of tartaric acid disappeared completely (10-12 hours). While stirring continued, 2 g of sodium acetate was added in order to neutralize the catalyst. The reaction mixture was transferred to a Claisen flask, vinyl acetate was distilled off under the vacuum of a water pump, and the reaction products were then distilled off at a residual pressure of

1-3 mm. The following fractions were obtained:

Fraction I, b.p. 28-40° (2 mm); 105 g
Fraction II, b.p. 40-120° (2 mm); 4 g
Fraction III, b.p. 120-130° (2 mm); 50 g

A resinous residue, insoluble in benzene and acetone, remained in the flask.

Fraction I was treated with aqueous sodium carbonate to neutralize acetic acid; it was then washed with water, dried over calcium chloride, and distilled from a Favorskii flask. The product, b.p. 60-61° (10 mm), had n_D^{20} 1.4021; d_4^{20} 1.071; found MR 33.21; calculated for $C_6H_{10}O_4$ MR 33.45.

These constants correspond to ethylidene diacetate; yield 45 g.

Fraction III was treated with anhydrous sodium carbonate in order to remove acetic acid and was then distilled from a Favorskii flask. The product, b.p. 127-128° (2 mm) had n_D^{20} 1.4516; d_4^{20} 1.252; found MR 43.60; calculated for divinyl tartrate MR 44.87.

Found %: C 47.94; 47.66; H 5.03; 5.08. $C_8H_{10}O_6$. Calculated %: C 47.5; H 4.95.

Determination of active hydrogen (by Terent'ev's method):

Found: H_{act} 0.927; 0.918
Calculated: H_{act} 0.99

The yield was 30-31 g (30-31 %). In the hydrolysis of the divinyl tartrate the values found by titration for the acid were 100.2 and 100.6 (% of the theoretical value).

SUMMARY

Divinyl tartrate was synthesized.

LITERATURE CITED

[1] R. L. Adelman, J. Am. Chem. Soc. 75, 2678 (1953).

[2] R. L. Adelman, J. Org. Chem. 14, 1057 (1949).

[3] J. Oil Chemists Soc. Japan 1, 76-79 (1952); C. A. 47, 3232 (1953).

[4] M. F. Shostakovskii, B. I. Mikhant'ev, and N. N. Ovchinnikova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 556.*

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PREPARATION OF HEXACHLOROBUTADIENE

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Hexachlorobutadiene $CCl_2 = CCl - CCl = CCl_2$ (V) is an excellent solvent for many organic substances and, owing to its chemical stability, it has found extensive application in modern technology. Papers have appeared which describe several possible ways of synthesizing hexachlorobutadiene (V) [1], and there are some patents which briefly report the preparation of particular intermediate compounds in the synthesis of (V) [2]. It was of interest to investigate also other ways of synthesizing this technologically valuable substance from available raw material. Thus, in a previous communication from our laboratory [3] we showed that hexachlorobutadiene (V) can be prepared from butadiyne. We considered that it would be of interest also to verify the possibility of obtaining (V) from 2-butyne-1,4-diol in the following way:

$$CH_2OH - C \equiv C - CH_2OH \xrightarrow{SOCl_2} \underset{(I)}{CH_2Cl - C \equiv C - CH_2Cl}$$

$$\xrightarrow[CCl_4]{Cl_2} \underset{(II)}{CH_2Cl - CCl_2 - CCl_2 - CH_2Cl} \quad (1)$$

$$\xrightarrow[KOH,\ CH_3OH]{-2HCl} \underset{(III)}{CHCl = CCl - CCl = CHCl} \quad (2)$$

$$\xrightarrow[SbCl_5,\ CCl_4]{Cl_2} \underset{(IV)}{CHCl_2 - CCl_2 - CCl_2 - CHCl_2} \quad (3)$$

$$\xrightarrow[NaOH,\ CH]{-2HCl} \underset{(V)}{CCl_2 = CCl - CCl = CCl_2} \quad (4)$$

The complete sequence has not been reported in the literature, although separate stages of it are known.

1,4-dichloro-2-butyne (I) was prepared by Johnson's method [4] in 86 % yield. The chlorination of (I) has not been described previously. There is only one reference in the literature to the addition of chlorine to a disubstituted acetylene, namely the preparation of the tetrachloride of diphenylacetylene by the saturation of a chloroform solution of diphenylacetylene at 0° with chlorine [5]. It was found that, under these conditions, chlorine did not add to 1,4-dichloro-2-butyne. We succeeded in bringing about the reaction in about 98 % yield by the chlorination of (I) in carbon tetrachloride solution at a temperature of from -40° to -50°, and in about 75 % yield by the same reaction at 60° [the yield refers to crystalline hexachlorobutane (II)]. 1,2,3,4-Tetrachlorobutadiene (III) was obtained by the dehydrochlorination of (II) with the aid of methanolic KOH in accordance with the US patent [1]. This reaction is complex, and the yield of crystalline (III) was 30-40 %. Apart from this solid product, a considerable amount of liquid was obtained; it appeared to be a mixture of isomers and was not investigated further. Later, by a slight modification of the method indicated in the patent, we succeeded in obtaining crystalline tetrachlorobutadiene (III) in 50 % yield. Chlorination of (III) in presence of a catalyst ($SbCl_5$) at 30-50° finally gave hexachlorobutene, and not octachlorobutane (IV) as indicated in a German patent [2]:

$$CHCl = CCl - CCl = CHCl \xrightarrow[SbCl_5,\ CCl_4]{Cl_2} CHCl_2 - CCl = CCl - CHCl_2.$$
(VI)

We synthesized octachlorobutane (IV) by the action of liquid chlorine on the crystalline substance (III) under pressure in sealed tubes exposed to ultraviolet radiation [3]. The yield of the crystalline octachlorobutane (IV) was 91 %. The last stage in the preparation of hexachlorobutadiene (V)[the dehydrochlorination of octachlorobutane (IV)] has been carried out previously [3].

EXPERIMENTAL

1,4-Dichloro-2-butyne (I) and 1,2,3,4-tetrachlorobutadiene (III) were prepared as indicated previously [2, 4]; (I) had b.p. 71-72° (25 mm) and n_D^{20} 1.5050; and (III) had m.p. 47-48°.

Chlorination of 1,4-Dichloro-2-butyne (I)

a) A solution of 20 g of 1,4-dichloro-2-butyne in 120 ml of carbon tetrachloride was placed in a three-necked round-bottomed flask fitted with mechanical stirrer, thermometer, and reflux condenser. The solution was warmed to 60° and stirred vigorously while a powerful stream of chlorine was passed. Further chlorination was carried out at 65-67° for 3-4 hours with continuous passage of chlorine. After removal of carbon tetrachloride we obtained 32 g (74.4 %) of hexachlorobutane (II) in the form of white crystals and 5.5 g of a liquid having n_D^{20} 1.5270, which we did not investigate further. According to the literature, hexachlorobutane has m.p. 105-106° [6], 107° [2].

b) A solution of 10 g of 1,4-dichloro-2-butyne in 50 ml of carbon tetrachloride was added dropwise over a period of 30 minutes to a vigorously stirred solution of 70 g of chlorine in 100 ml of carbon tetrachloride at -60°. The mixture was stirred for six hours at a temperature of from -45° to -40° and then left overnight. On the next day stirring was continued for 90 minutes at 40-50°. Solvent was removed and we obtained 21 g (97.6 %) of hexachlorobutane (II), which showed no depression of melting point in admixture with the above-described sample. Under these conditions no liquid product was obtained.

Chlorination of 1,2,3,4-Tetrachlorobutadiene (III)

a) A powerful stream of chlorine was passed at room temperature into a solution of 7.8 g of tetrachlorobutadiene (III) in 100 ml of carbon tetrachloride to which 1 g of $SbCl_5$ had been added. After 30 minutes the temperature of the mixture was raised to 50-55° and passage of chlorine was continued for a further 3-4 hours. After removal of carbon tetrachloride we obtained 5 g (50 %) of 1,1,2,3,4,4-hexachloro-2-butene (VI) in the form of colorless rhombs, m.p. 76-77°. After being recrystallized twice from alcohol, (VI) melted at 77.5-78° and showed no depression in melting point in admixture with a known sample [3].

Found %: C 18.03; 17.86; H 0.84; 0.74; Cl 81.27; 81.30. $C_4H_2Cl_6$. Calculated %: C 18.28; H 0.77; Cl 80.95.

The literature [2] gives m.p. 80° for the m.p. of hexachlorobutene (VI).

b) A solution of 8.6 g of tetrachlorobutadiene (III) in 35 ml of carbon tetrachloride was placed in a glass tube and was cooled to -70° and saturated with chlorine (increase in weight 60 g), after which the tube was sealed. The reaction mixture was left for 15-20 hours at room temperature, and then was exposed to ultraviolet radiation for 30 hours. After removal of excess of chlorine and solvent we obtained 13.7 g (91 %) of octachlorobutane (IV), which showed no depression of melting point in admixture with a known sample [3].

SUMMARY

1. It was shown that it is possible to prepare hexachlorobutadiene from 2-butyne-1,4-diol.

2. The conditions for the chlorination of 1,4-dichloro-2-butyne were studied; 1,2,2,3,3,4-hexachlorobutane (II) was obtained in quantitative yield.

3. It was shown that, depending on reaction conditions, the chlorination of 1,2,3,4-tetrachlorobutadiene can give either 1,1,2,3,4,4-hexachloro-2-butene or 1,1,2,2,3,3,4,4-octachlorobutane (IV).

LITERATURE CITED

[1] E. T. McBee, H. B. Haas and E. Pierson, Ind. Eng. Chem. 33, 181 (1941); E. T. McBee and R. E. Hatton, Ind. Eng. Chem. 41, 809 (1949); O. Fruhrirth, Ber. 74, 1700 (1941); I. A. Krynitsky and H. W. Carhart, J. Am. Chem. Soc. 71, 816 (1949); A. Roeding, Ann. 574, 122 (1951); V. M. Zhulin, Candidate's Thesis, Moscow, 1956.

[2] R. Decker and H. Holz, German Patent, 836641 (1952); C. A. 5421a (1953); P. A. Wiseman, US Patent 122, 130; C. A. 10, 674 (1952); 7533 (1953); E. Müller and T. Hunther, Ber. 64, 589 (1931).

[3] M. F. Shostakovskii, E. S. Shapiro and L. I. Shmonina, Proc. Acad. Sci. USSR (in the press).

[4] A. W. Johnson, J. Am. Chem. Soc. 1009 (1946).

[5] V. Redzko, J. Russ. Phys. Chem. Soc. 21, 421 (1889).

[6] P. A. Wiseman, British Patent 675372; C. A. 10, 674 (1952).

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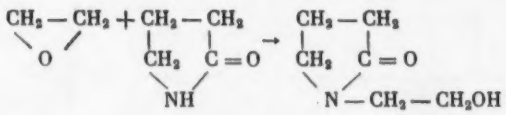
INVESTIGATION OF LACTONES AND LACTAMS

COMMUNICATION 11.* CONDENSATION OF ETHYLENE OXIDE WITH LACTAMS

M. F. Shostakovskii and F. P. Sidel'kovskaia

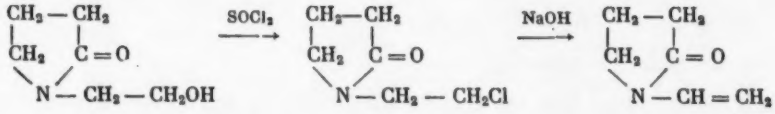
The condensation of epoxides with lactams has not been described in the literature.** There are brief references to the addition of ethylene oxide, epichlorohydrin, and glycidol to some compounds that are close in structure to lactams, e.g. acetamide, benzamide [3], and phthalimide [4].

In the present investigation we studied the reaction of ethylene oxide with 2-pyrrolidinone and with caprolactam. The conditions of the reaction were investigated in greater detail in the case of 2-pyrrolidinone. The process was carried out at 20°, 60°, and 200° in presence and absence of water, methanol, or sulfuric acid and also with various relative amounts of reactants. At 20° and 60° ethylene oxide did not react with 2-pyrrolidinone, but at 200-210° (the experiments were carried out in steel autoclaves) reaction occurred with formation of 1-(2--hydroxyethyl)-2-pyrrolidinone, which has been synthesized previously from butyrolactone and 2-aminoethanol [5].



Investigation of various reaction conditions showed that the yield of the (hydroxyethyl)pyrrolidinone is raised by increasing the amount of ethylene oxide taken for reaction. The best results were obtained at a ratio of pyrrolidinone to ethylene oxide of 1 : 2. Further increase in the excess of ethylene oxide was of no appreciable advantage. The yield was increased also by the addition of small amounts (up to 3 %) of water or alcohol to the reaction mixture; resin formation was then suppressed and it was easier to isolate the product. Addition of water in large amounts had an unfavorable effect on the yield of the (hydroxyethyl)pyrrolidinone.

The structure of the resulting 1-(2-hydroxyethyl)-2-pyrrolidinone was proved by the identity of its constants with those given in the literature and by certain reactions: with thionyl chloride it gave the previously described 1-(2-chloroethyl)-2-pyrrolidinone [5], and heating of this with alkali resulted in elimination of HCl and formation of 1-vinyl-2-pyrrolidinone:



We studied the reaction between ethylene oxide and caprolactam under conditions similar to those required for the reaction of ethylene oxide with 2-pyrrolidinone (with and without additions of water or alcohol). However, we did not succeed in isolating the corresponding hydroxyethyl derivative. Under mild conditions (low temperature) the caprolactam was recovered unchanged, and under severe conditions (200-210°) a brown powder was ob-

* For Communication 10 see [1].

** After this paper had been submitted for publication a paper appeared on the addition of lactams to (epoxyethyl)benzene [2].

tained. This was probably a mixture of caprolactam polymers. It is known, for example, that at high temperature, particularly in presence of small amounts of water or alcohol, the caprolactam ring opens with formation of the equilibrium polymerization product, consisting of linear polymer containing 6-aminohexanoic acid, unchanged lactam, and cyclic oligomers [6].

EXPERIMENTAL*

Condensation of Ethylene Oxide with 2-Pyrrolidinone. The necessary amounts of 2-pyrrolidinone and liquid ethylene oxide (in some experiments with addition of water, methanol, or sulfuric acid) were introduced into a 500-ml rotating steel autoclave. The autoclave was heated for ten hours at 200-210°. At first there was a rise in pressure to 20 atm, but there followed a rapid fall to 3-5 atm and the pressure remained in this range throughout the remainder of the process. The product, which was usually a dark-colored viscous mass, was vacuum-fractionated.

Example. The product obtained by reaction between 30 g (0.35 mole) of 2-pyrrolidinone and 15 g (0.35 mole) of ethylene oxide (with the addition of 1 ml of water) was dried with sodium sulfate and vacuum-fractionated; it gave:

Fraction I, b.p. 98-109° (3 mm); n_D^{21} 1.4705; 19.0 g (the temperature rose rapidly to 125°)
Fraction II, b.p. 125-150° (3 mm); n_D^{21} 1.4930; 17.0 g
Fraction III, b.p. 160-165° (3 mm); n_D^{21} 1.4920; 3.1 g
Resin 3.4 g

TABLE

Results of Experiments on the Addition of Ethylene Oxide to 2-Pyrrolidinone at 200-210°

No.	Molar ratio of pyrrolidinone to ethylene oxide	Additive and amount (% on pyrrolidinone)	Duration of heating (hours)	Yield of 1-(2--hydroxyethyl)--2-pyrrolidinone	Amount of resin (% on total mass of reactants)
1	1 : 1	–	10	16	40
2	1 : 1	CH_3OH – 3%	10	20.3	33
3	1 : 1	H_2O – 3%+ + 2 drops of H_2SO_4	10	14	25
4	1 : 1	H_2O – 3%	10	18.7	11
5	1 : 1	H_2O – 3%	15	18.7	23
6	1 : 1	H_2O – 15%	15	13.2	13
7	1 : 2	H_2O – 3%	10	44	25
8	1 : 2	H_2O – 10%	10	21	16

After two further fractionations, Fraction I gave 13 g of unchanged 2-pyrrolidinone, b.p. 102-104° (3 mm) and Fractions II and III gave 10 g of 1-(2-hydroxyethyl)-2-pyrrolidinone, b.p. 140-142° (3 mm); n_D^{20} 1.4950; d_4^{20} 1.1435; yield 24.5%. The literature [5] gives b.p. 140-142° (3.5 mm). Active hydrogen (%) (determined by Tserevitinov's method) was 0.68; 0.67 (calculated 0.77).

The results of other experiments are given in the table.

Thionyl chloride (26 g) was added to a cooled stirred solution of the 1-(2-hydroxyethyl)-2-pyrrolidinone (28.5 g) in benzene (25 ml) (the temperature did not exceed 15°). The mixture was set aside overnight, solvent was distilled off, and fractionation then gave 29.9 g (90 %) of 1-(2-chloroethyl)-2-pyrrolidinone, b.p. 107° (4 mm). After being redistilled it had b.p. 97° (2 mm); n_D^{20} 1.4950, d_4^{20} 1.1932; found MR 36.08; calculated MR 36.53. The literature gives b.p. 115-116° (5 mm).

Determination of chlorine content: a sample of the 1-(2-chloroethyl)-2-pyrrolidinone (0.2-0.25 g) was

*Laboratory worker T. Ia. Lipniak and T. T. Dumpis, student of the Leningrad State University, took part in the experimental work.

boiled with 20 ml of 10 % NaOH for one hour, the solution was neutralized with 20 ml of 10% H_2SO_4, and chloride was titrated by Volhard's method.

Found %: Cl 24.28; 24.26. $C_6H_{12}OCl$. Calculated %: Cl 24.04.

SUMMARY

1. The condensation of ethylene oxide with 2-pyrrolidinone was studied. It was shown that 1-(2-hydroxyethyl)-2-pyrrolidinone was formed.

2. In order to prove the structure of the (hydroxyethyl)pyrrolidinone it was converted into the (chloroethyl)pyrrolidinone by treatment with thionyl chloride. The yield of 1-(2-chloroethyl)-2-pyrrolidinone was about 90 %.

LITERATURE CITED

[1] M. F. Shostakovskii, E. S. Shapiro, and F. P. Sidel'kovskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1958, 69.*

[2] W.Liegenbein and W. Franke, Ber. 90, 2291 (1957).

[3] F. G. Ponomarev, Bull. All-Union Mendeleev Chem. Soc. No. 5, 33, 1941; Trans. Voronezh Univ. 17, 113, 1950.

[4] Gabriel and Ohle, Ber. 50, 820.

[5] B. Puetzer, L. Katz and L. Horwitz, J. Am. Chem. Soc. 74, 4959 (1952).

[6] P. H. Hermans, J. Appl. Chem. No. 9, 493 (1955).*

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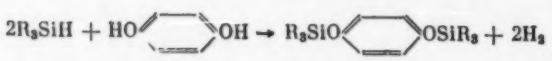
CATALYTIC DEHYDROCONDENSATION OF TRIALKYL- AND TRIARYL-SILANES WITH HYDROXY, OXO, AND POLYHYDROXY ORGANIC COMPOUNDS

B. N. Dolgov, Iu. I. Khudobin and N. P. Kharitonov

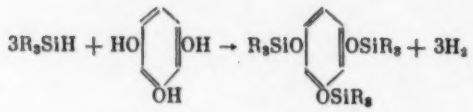
There is information in the literature on the possibility of condensing trialkylsilanes with monohydric alcohols and with amines in presence of small amounts of alkali metals [1, 2], and also with monocarboxylic acids in presence of a mixture of iodine and aluminum [3]. We have developed a general method for introducing trialkyl- or triaryl-siloxy groups into any organic molecules containing hydroxy, oxo, or polyhydroxy groups. Suitable catalysts were found in various metal halides, the action of which has not been reported in the literature. The best results were obtained with additions of 0.1-3 % (on the amount of trialkyl- or triaryl-silane) of the halides of Ni, Co, Cr, Ge, Zn, Sn, and others.

The reactions were carried out by simply heating a mixture of the components; no by-products were formed, and yields of 90-95 % were obtained. The progress and rate of the reaction can be readily checked by measuring the liberated hydrogen. The reactions proceed in accordance with the following very simple equations:

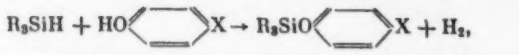
$$R_3SiH + HOR' \rightarrow R_3SiOR' + H_2$$



$$2R_3SiH + HO\text{-}C_6H_4\text{-}OH \rightarrow R_3SiO\text{-}C_6H_4\text{-}OSiR_3 + 2H_2$$



$$3R_3SiH + HO\text{-}C_6H_3(OH)\text{-}OH \rightarrow R_3SiO\text{-}C_6H_3(OSiR_3)\text{-}OSiR_3 + 3H_2$$



$$R_3SiH + HO\text{-}C_6H_4\text{-}X \rightarrow R_3SiO\text{-}C_6H_4\text{-}X + H_2,$$

in which X = F, Cl, Br, I, etc.

The table gives physicochemical properties, yields, and analytical data for trialkylsilyl derivatives of some hydroxy, oxo, and polyhydroxy compounds. Detailed investigations of the catalytic dehydrocondensation of trialkyl- and triaryl-silanes with hydroxy, oxo, and polyhydroxy organic compounds will be published in subsequent communications. We here describe some typical experiments.

EXPERIMENTAL

Synthesis of 1,3,5-Tris(dibutylethylsiloxy)benzene. A mixture of 293 g (1.7 moles) of dibutylethylsilane, 63 g of phloroglucinol, and 0.5 g (0.0039 mole) of anhydrous cobalt chloride was heated at 145-165° until hydrogen ceased to be evolved (seven hours). Distillation of the reaction product gave 299.6 g (94 %) of 1,3,5-tris(dibutylethylsiloxy)benzene, b.p. 287-289° (4 mm). After redistillation it had b.p. 283° (3 mm); d_4^{20} 0.9148; n_D^{20} 1.4769.

Synthesis of 1,3,5-Tribromo-2-(dibutylethylsiloxy)benzene. A mixture of 10.3 g (0.06 mole) of dibutylethylsilane, 16.5 g (0.05 mole) of tribromophenol, and 0.2 g (0.0011 mole) of anhydrous stannous bromide was heated at 210-240° until hydrogen ceased to be evolved (three hours). Distillation of the reaction product gave 24 g (96%) of 1,3,5-tribromo-2-(dibutylethylsiloxy)benzene, b.p. 259-262° (9 mm). After redistillation it had b.p. 261° (9 mm); d_4^{20} 1.4783; n_D^{20} 1.5458.

TABLE

Physicochemical Properties, Yields, and Analytical Data for Trialkylsilyl Derivatives of some Hydroxy, Oxo, and Polyhydroxy Compounds

No.	Compound	B. p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR (according to Vogel [4])		Analysis (%)						Molar ratio of trialkylsilane to organic compound	Catalyst	Amount of catalyst (moles % on trialkylsilane)	Duration of reaction (minutes)	Yield of product (%)
							Si		C		H						
					Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated					
1	Butoxydiethylmethylsilane	172.2(761.1)	0.8060	1.4125	53.89	54.25	15.85; 15.97	16.11	61.81 62.15	62.00	12.80 12.80	12.78	0.1 : 0.2	$ZnCl_2$	1.5	30	86
2	Dibutylethylphenoxysilane	291.6 (760)	0.9074	1.4830	83.24	83.03	10.61; 10.67	10.62	—	—	—	—	0.12 : 0.1	$GeCl_4$	4.2	30	93
3	(Dibutylethylsiloxy)guaiacol	170 (4)	0.9440	1.4854	89.48	89.46	9.73; 9.67	9.54	—	—	—	—	0.12 : 0.1	$NiCl_2$	6.4	100	90
4	(Dibutylmethylsiloxy)thymol	152 (5)	0.8924	1.4800	97.59	—	9.12; 9.14	9.16	—	—	—	—	0.12 : 0.1	$SnCl_2$	4.4	285	90
5	(Dibutylethylsiloxy)borneol	185.5 (5)	0.8936	1.4643	100.32	—	8.62; 8.70	8.65	—	—	—	—	0.12 : 0.1	$NiCl_2$	6.4	100	93
6	Dibutylmethyl-1-naphthyloxysilane	194 (9)	0.9659	1.5330	96.30	—	9.38; 9.44	9.35	—	—	—	—	0.12 : 0.1	$SnCl_2$	4.4	180	90
7	Dibutylmethyl-2-naphthyloxysilane	183 (4)	0.9635	1.5334	96.86	—	9.46; 9.43	9.35	—	—	—	—	0.12 : 0.1	$SnCl_2$	4.4	150	92
8	(Ethyldiisobutylsiloxy)-o-cresol	140.5 (6)	0.9088	1.4846	87.67	87.67	10.05; 10.12	10.08	—	—	—	—	0.12 : 0.1	$SnCl_2$	4.4	1785	86
9	Diisopentylmethyl-m-tolyloxysilane	293.2(751.1)	0.8876	1.4740	92.74	92.32	9.79; 9.89	9.61	74.20 74.41	73.90	11.01 11.16	11.03	0.12 : 0.1	$SnCl_2$	4.4	130	99
10	Ethyldiisopentyl-p-tolyloxysilane	316.5(756.4)	0.8938	1.4773	96.97	96.97	9.09; 9.05	9.16	—	—	—	—	0.12 : 0.1	$NiCl_2$	6.4	9	94
11	o-Bis(dibutylethylsiloxy)benzene	253 (7)	0.9151	1.4810	139.71	139.87	12.49; 12.43	12.46	—	—	—	—	0.12 : 0.05	$NiCl_2$	3.2	40	97
12	m-Bis(dibutylethylsiloxy)benzene	211.5 (3)	0.9136	1.4800	140.19	139.87	12.40; 12.49	12.46	69.05 68.88	69.26	11.09 11.29	11.18	1.1 : 0.5	$SnCl_2$	0.53	155	96
13	p-Bis(dibutylethylsiloxy)benzene	221 (3)	0.9131	1.4795	140.14	139.87	12.50; 12.45	12.46	—	—	—	—	1.1 : 0.5	$CoCl_2$	0.35	720	89
14	1,3,5-Tris(dibutylethylsiloxy)benzene	264 (1) 432 (760)	0.9148	1.4769	196.79	196.72	13.30; 13.25	13.22	68.11 68.17	67.85	11.49 11.51	11.39	1.0 : 0.3	$NiCl_2$	0.77	60	94
15	Dibutylmethylsilyl ester of 2,4-bis(dibutylmethylsiloxy)benzoic acid	300 (5.5)	0.9420	1.4785	—	—	13.62; 13.72	13.52	—	—	—	—	0.2 : 0.05	$NiCl_2$	1.9	20	96
16	1-(Tributylsiloxy)-4-chlorobenzene*	196 (3)	0.9688	1.4892	97.46	97.16	8.65; 8.68	8.59	—	—	—	—	0.06 : 0.05	$SnCl_2$	4.4	38	98
17	1-Bromo-4-(dibutylethylsiloxy)benzene**	194 (3)	1.1168	1.5015	90.74	90.71	8.15; 8.20	8.17	—	—	—	—	0.06 : 0.05	$SnCl_2$	4.4	55	97
18	Tribromo(dibutylethylsiloxy)benzene***	260 (9)	1.4783	1.5458	—	—	5.59; 5.68	5.60	—	—	—	—	0.16 : 0.05	$SnBr_2$	1.83	180	96

* Calculated Cl 10.84 %; found Cl 11.00; 10.85 %.

** Calculated Br 23.27 %; found Br 23.20; 23.36 %.

*** Calculated Br 47.83 %; found Br 47.90; 47.65 %.

SUMMARY

1. A general catalytic method was developed for the preparation of trialkyl- and triaryl-silyl derivatives of organic hydroxy, oxo, and polyhydroxy compounds.

2. It was found that the best catalysts for the reaction are halides of Ni, Co, Cr, Ge, Zn, and Sn. Eighteen trialkylsilyl derivatives of hydroxy, oxo, and polyhydroxy compounds were synthesized in yields of up to 95 %, and their physicochemical properties were determined.

3. It was shown that some trialkyl- and triaryl-silyl derivatives of organic hydroxy and polyhydroxy compounds freeze below -50° and boil without decomposition above 500° (760 mm). These compounds can be used as heat carriers.

LITERATURE CITED

[1] B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov, J. Gen. Chem. 24, 1178 (1954).*

[2] B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov, J. Gen. Chem. 24, 678 (1954).*

[3] B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov, J. Gen. Chem. 24, 861 (1954).*

[4] A. J. Vogel, I. Chem. Soc. 1948, 1833, A. J. Vogel, W. T. Cresswell, G. Jeffery and J. Leicester, J. Chem. Soc. 1952, 514.

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HETEROCHAIN POLYAMIDES

COMMUNICATION 5. KINETICS OF THE FORMATION OF MIXED POLYAMIDES FROM 1,6-HEXANEDIAMINE AZELAATE AND 6-CAPROLACTAM

V. M. Kharitonov, T. M. Frunze and V. V. Korshak

We have previously reported results on the kinetics of the polycondensation of 1,6-hexanediamine adipate and azelaate [1], the kinetics of the polymerization of 6-caprolactam [2], and the kinetics of the formation of mixed polyamides from the 1,6-hexanediamine salts of azelaic and adipic acids [3]. In the present investigation we studied the kinetics of the formation of mixed polyamides from 1,6-hexanediamine azelaate and 6-caprolactam. The reaction was carried out in the manner described previously [1] in cresol (mixture of isomers) solution at 205°; the total concentration of monomers in the original solutions was 32.37%. The results are shown in Figures 1-3. As reaction proceeds, increases are observed in the yield of copolymer and in its molecular weight (Fig. 1). These quantities are greatly affected by the relative amounts of reactants taken. Thus, change in the molar ratio of 6-caprolactam to 1,6-hexanediamine azelaate (HA) from 7 : 1 to 3 : 1, i.e. increase in the HA content, results in increase in the yield and molecular weight of the polyamide obtained. 6-Caprolactam reacts much more slowly than HA. In the course of two hours 6-caprolactam reacts to the extent of 30-35 %, whereas HA reacts to the extent of more than 90% (Fig. 2).

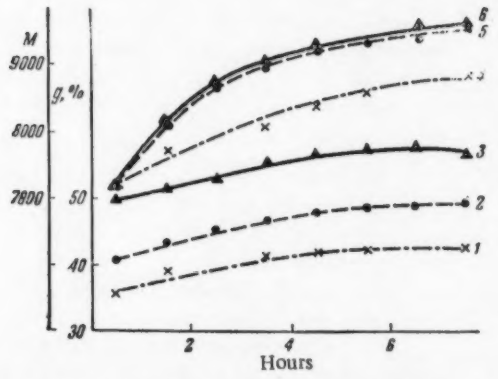

Fig. 1. Variation in yield (g) and molecular weight (M) of copolymer in the copolymerization of HA with 6-caprolactam for various ratios (φ) of caprolactam to HA: 1, 4) g and M respectively for $\varphi = 7$; 2, 5) g and M respectively for $\varphi = 5$; 3, 6) g and M respectively for $\varphi = 3$.

In the early stages of reaction in which HA is the more rapidly reacting component, there is an increase in the amount of 6-caprolactam that enters the reaction. Simultaneously, substantial changes are occurring in the relative contents of HA and 6-caprolactam residues in the polymer formed. This can be seen particularly clearly when the products obtained from different proportions of reactants are compared. At first the copolymer contains a greater relative amount of HA residues, and then, as the process proceeds, the amount of caprolactam residues increases until a condition is reached which corresponds to equilibrium for the given relative amounts of reactants (Fig. 2).

In the course of the reaction the amount of products of low molecular weight diminishes, and the content of these products in the copolymer depends on the amount of HA in the original mixture, for the greater the HA content the smaller the amount of low-molecular-weight products formed as a result of reaction (Fig. 3). Growth of polyamide chains proceeds in two ways: by reaction between growing chains and molecules of the original substances, and by condensation among the polyamide molecules. In the first stages of the reaction there is an increase in the number of polyamide molecules, but a reduction in this number is then observed, which shows that reaction among the polyamide molecules themselves already plays an important part in the general course of the

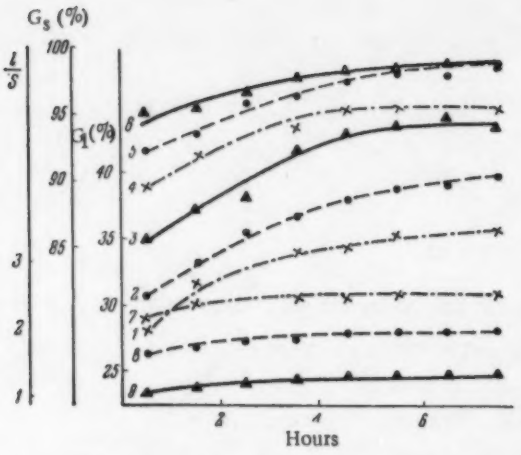

Fig. 2. Change in the course of reaction of the amounts of caprolactam (Gl) and HA salt (Gs) that have reacted and of the relative amounts of these substances combined in the copolymer (1/s) for various relative amounts (φ) of the reactants: 1, 4, 7) Gl, Gs, and 1/s respectively for $\varphi = 7$; 2, 5, 8) Gl, Gs, and 1/s respectively for $\varphi = 5$; 3, 6, 9) Gl, Gs, and 1/s respectively for $\varphi = 3$.

process in the early stages. This behavior is reflected both in the rapid reduction in the content of soluble products, and in the reduction in the number of polyamide molecules (Fig. 3). The coefficient of polydispersity of the polyamide formed falls continuously as reaction proceeds, which indicates increased homogeneity of the polyamide, i.e. the accumulation of macromolecules of similar size. This indicates also that degradation and exchange reactions are occurring in the way that is characteristic for the polycondensation process [4].

From the results we may conclude that the two initial reactants react at different rates. The salt HA, which has the lower activation energy, reacts more rapidly than 6-caprolactam, which has the higher activation energy [1, 2]. Also, the salt HA is an activator of the polymerization of 6-caprolactam. Hence, the amount of caprolactam entering into reaction in the first stage depends also on the amount of HA. In the first stage the growth of the polyamide macromolecules proceeds both by reaction of HA with caprolactam and by reaction of the macromolecules already formed with one another. As the process proceeds, the first type of reaction takes a secondary position and the second type becomes more and more of primary importance.

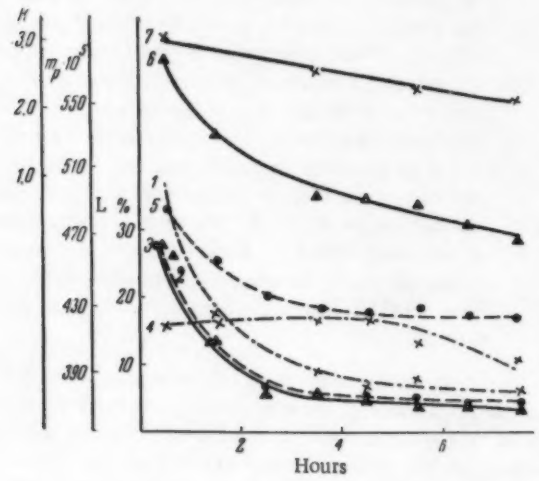

Fig. 3. Changes in the content of alcohol-soluble low-molecular-weight compounds (L) in the copolymer and in the number of moles of polyamide (m_p) in the copolycondensation process for various molar ratios of 6-caprolactam to the salt HA (φ) in the original mixture: 1, 4) L and m_p respectively for $\varphi = 7$; 2, 5) L and m_p respectively for $\varphi = 5$; 3, 6) L and m_p respectively for $\varphi = 3$; 7) change in the coefficient of polydispersity K for $\varphi = 7$

Simultaneously with chain growth, exchange reactions among macromolecules and between macromolecules and the original reactants become more and more important. As a result of these reactions, the copolymer formed becomes ever richer in 6-caprolactam residues, and a product is finally obtained in which the relative amounts of the repeating units correspond to the original composition of the reaction mixture, as is shown by carrying out the reaction in absence of solvent, when we obtain up to 99 % yield of polyamide containing residues of the original reactants in the same proportion as that taken for the original mixture.

The results confirm the correctness of the views that we have expressed previously [3, 5], namely, that the ultimate composition of a mixed polyamide is determined not by the kinetics of the process, as it is in the case of free-radical polymerization, but by the relative amounts of the reactants and the conditions under which equilibrium is attained.

SUMMARY

1. It was shown that, in the copolycondensation of 1,6-hexanediamine azelaate with 6-capro-

lactam, the more active component (1,6-hexanediamine azelaate) is the main reactant in the early stages, and it is only in the later stages of reaction that the composition of the original reaction mixture and that of the polyamide formed become identical.

2. It was shown that, in the process of forming mixed polyamides, the composition of the polymers formed in the final stages of the process is determined by the relative amounts of the original substances, and not by the kinetics of individual stages of the process.

LITERATURE CITED

[1] V. M. Kharitonov, T. M. Frunze and V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1002.*

[2] V. M. Kharitonov, T. M. Frunze and V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1134.*

[3] V. M. Kharitonov, T. M. Frunze and V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1136.*

[4] V. V. Korshak and V. A. Zamiatina, Proc. Acad. Sci. USSR 59, 909 (1948).

[5] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 563.*

Institute of Heteroorganic Compounds of
the Academy of Sciences of the USSR and
All-Union Artificial Fiber Research Institute

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* Original Russian pagination. See C. B. Translation.

LETTERS TO THE EDITOR

TRISTRIALKYLSILYL PHOSPHITES

Dear editor,

Organosilicon esters of oxygen acids of quinquevalent phosphorus have been well studied. On the other hand, the corresponding tervalent phosphorus derivatives are quite unknown. We have developed two methods of synthesizing compounds of this type, namely tristrialkylsilyl phosphites.

The first is based on reaction of PBr_3 with alkoxytrialkylsilanes:

$$3R_3SiOR' + PBr_3 \rightarrow (R_3SiO)_3P + 3R'Br.$$

The synthesis was effected simply by distilling a mixture of PBr_3 with excess of the alkoxytrialkylsilane in which 0.5-0.6 mole % of a catalyst such as $ZnCl_2$, $FeCl_3$, or $SnCl_2$ was dissolved. First, 75-100 % of the theoretical amount of R'Br was distilled off, and fractionation then gave the tristrialkylsilyl phosphite (yield about 30%).

The other method is based on the splitting of hexaalkyldisiloxanes, taken in considerable excess, by means of phosphorus trihalides in presence of the above-mentioned catalysts:

$$3R_3SiOSiR_3 + PX_3 \rightarrow (R_3SiO)_3P + 3R_3SiX,$$

the procedure being similar to before. When PBr_3 is used the yields of tristrialkylsilyl phosphites are 25-30 %.

We shall shortly publish a detailed report on the two new reactions, the physical and chemical properties of the tristrialkylsilyl phosphites, and their vibrational spectra.

M. G. Voronkov
Iu. I. Skorik

Institute of Silicate Chemistry of the
Academy of Sciences of the USSR

Received October 24, 1957

Dear editor,

As a result of a study of the infrared spectra of compounds of the types R − Li and R − O − Li, we have detected the formation of intermolecular lithium bonds $\ldots C^{-\delta}-Li^{+\delta}\ldots C^{-\delta}-Li^{+\delta}$ and $\ldots O^{-\delta}-Li^{+\delta}\ldots O^{-\delta}-Li^{+\delta}\ldots$ Comparison of spectra of vapors, solutions, and powders in petroleum jelly and analysis of the forms of vibration of the molecules enabled us to determine the frequencies of the valence vibrations of C − Li groups, both free and also bound in the formation of a lithium bond (Table).

TABLE

Compound	$\nu_{C-Li(O-Li)}$ (free) cm^{-1}	ν ..O − Li.. ..(..O − Li) (associated) cm^{-1}	$\frac{\Delta\nu}{\nu_0}$ %
CH_3Li (vapor)	1052 m.	–	–
Same (crystal)	1060 m.	820 s. b.	19
C_2H_5Li (vapor)	1061 s.	–	–
Same (crystal)	1056 s.	882 s. b.	16
Same + benzene (0.8 N)	1050 w.	918 s. b.	
		875 m.	12
Same + benzene (0.1 N)	1050 w.	920 m.	
		875 m.	12
Same + hexane (1 N)	1052 s.	915 m.	13
Same + hexane (0.27 N)	1058 m.	–	–
C_6H_5Li (vapor)	1029 s.		
	1045 m.	–	–
Same (crystal)	1039 s.	838 s. b.	19
$C_{12}H_{25}Li$ + hexane (0.53 N)	1052 m.	927 s. b.	12
Same + hexane (0.13 N)	1058 s.	930 w.	13
p-$CH_3C_6H_4Li$ (crystal)	987 m.	833 s. b.	15
α-$C_{10}H_7Li$ (crystal)	940 m.	828 s. b.	12
CH_3OLi (crystal)	~1400 s.	840 s. b.	35

Denotations: s - strong; w- weak; m- medium; b -broad

The intermolecular lithium bond $-C^{-\delta}\ldots Li^{+\delta}-$ is strong in spite of the fact that it is formed without the participation of acceptor-donor interaction. The bond $-Li^{+\delta}\ldots O^{-\delta}-$ is still stronger. The formation of strong intermolecular lithium bonds is a manifestation of the special nature of the lithium atom (small radius, comparatively low ionization potential, and high tendency to have a p orbital) which ensures the more active direct participation of its electron in intermolecular action as compared with the case of the hydrogen atom. R − Li molecules are associated differently in crystals (chains) and solutions (rings). The extent and character of association in solutions depend greatly on the nature of the solvent.

A. Rodionov, D. Shigorin
T. Talalaeva, K. Kocheshkov

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Received December 20, 1957

CURRENT EVENTS

EXTRAMURAL SESSION OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR

(Kazan, September 27-28, 1957)

The Division of Chemical Sciences held an extramural session in Kazan in honor of the eightieth birthday of the great organic chemist A. E. Arbuzov and the completion of fifty-five years of scientific and public activities by him. Aleksandr Erminingel'dovich Arbuzov is a full member of the Academy of Sciences of the USSR, a deputy of the Supreme Soviet of the USSR, a Hero of Socialist Labor, an honorary member of the All-union Mendeleev Chemical Society, a member of the Presidium of the Academy of Sciences of the USSR, and president of the Presidium of the Kazan Affiliated Institute of the Academy of Sciences of the USSR.

The first meeting of the Session took place on September 27 in the Assembly Hall of the V. I. Ul'ianov--Lenin University, Kazan. The enormous Assembly Hall of Kazan University, which holds about 700, was overflowing. The scientists and university and industrial workers that attended the Session came from Moscow, Leningrad, Irkutsk, Novosibirsk, Sverdlovsk, Gor'kii, Ufa, Minsk, Riga, Baku, Tashkent, Samarkand, Rostov, and other cities.

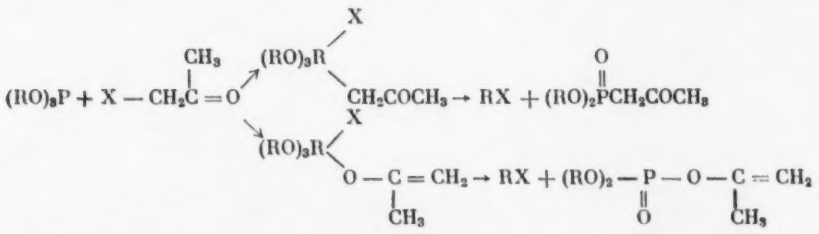
The meeting was opened by the deputy academician-secretary of the Division, Corr. Member Acad. Sci. USSR M. M. Shemiakin, who warmly welcomed Academician Arbuzov on behalf of the Division of Chemical Sciences. Academician A. E. Arbuzov then addressed the meeting, beginning with the words "In this day and hour, so memorable and significant for me, I wish to tell you briefly about my journey in the land of organophosphorus compounds." In an exceptionally interesting and enjoyable talk, illustrated by experimental demonstrations, he described the main stages of his creative journey. Interesting pages in the development of organophosphorus chemistry were laid open before the audience. While still quite young, A. E. Arbuzov was already investigating the structure of phosphorous acid and some of its organic derivatives. As a result of several years of sustained effort he obtained results of exceptional significance in this field: while studying the properties of the aliphatic phosphorous esters, which he had prepared for the first time, he discovered the remarkable reaction between phosphorous triesters and alkyl halides (particularly iodides) leading to the formation of alkylphosphonic esters, which are quinquevalent--phosphorus derivatives. As is well known, this reaction later became known as the "Arbuzov rearrangement." It is doubtful whether any organic chemist working on organophosphorus compounds can now be found who is not acquainted with this reaction and has not made use of it to some extent. Numerous investigations, both here and abroad, have been devoted to the mechanism of this reaction.

The next important stage was the investigation of the so-called Boyd's acid chloride, which was begun in 1928 by A. E. Arbuzov and his young student B. A. Arbuzov. As a result of this investigation, Boyd's views on the structure of the interesting compound that he had obtained were disproved and the way was opened to new lines of work in organophosphorus chemistry. Study of the structure of Boyd's acid chloride unexpectedly led to a new, elegant method of preparing free radicals of the triarylmethyl series. This reaction, which is accompanied by a color change, was demonstrated to the audience. In investigations of the preparation of free radicals by the action of triarylbromomethanes on alkali metal dialkyl phosphites, A. E. Arbuzov and his students discovered various new organophosphorus compounds, namely, hypophosphoric, pyrophosphoric, and pyrophosphorous esters. Many of the compounds synthesized later found extensive application in various fields of the national economy and medicine.

It is known that many organic derivatives of the pyro acids of phosphorus have insecticidal properties and are effective against pests that can devastate grain, fruit, and cotton crops and against the mites that attack domestic animals. Some organophosphorus compounds have been found to be very effective medicinals. "Phosarbin," which was synthesized in A. E. Arbuzov's laboratory, is used very successfully in the treatment of glaucoma; this preparation has saved many patients from blindness. Under the direction and with the participation of A. E. Arbuzov in the Institute of Chemistry of the Kazan Affiliated Institute of the Academy of Sciences of the USSR, numerous organophosphorus compounds having various valuable properties have been synthesized; the extensive introduction of the use of these in the national economy could have a great economic effect. Unfortunately, the manufacture of some of these preparations has not started, or is being carried on only to an insignificant extent. Speaking with some bitterness, A. E. Arbuzov pointed out the deficiencies in the organization of the introduction of the achievements of science into industry, and he expressed the hope that the recent reorganization of leadership in industry would help to open the way to the very rapid assimilation of scientific achievements in the national economy. He finished with the words: "At the present moment my students, the continuators of the line of scientific work to which I have devoted my life, are to be reckoned in dozens, probably many dozens, and here, of course, lies my reward as a scientist . . . . It is already difficult for me to climb the hill alone, and progress in science is always uphill; but in this difficult journey I am supported and helped by my students and coworkers, some of whom have already outdistanced me. This is not just a reward, it is the highest reward that a scientist could possibly receive."

Corr. Member Acad. Sci. USSR M. I. Kabachnik read an interesting paper on the "Tautomerism of Organophosphorus Compounds." He described the exceptionally important part played by A. E. Arbuzov in the discovery of the essential features of tautomerism in organophosphorus compounds. More than fifty years previously A. E. Arbuzov had for the first time raised the question of the tautomerism of organophosphorus compounds; already in his first investigations he showed that phosphorous acid and its dialkyl esters have the structures of quinquevalent phosphorus compounds, and he suggested the possibility of tautomerism in these compounds. Later, A. E. Arbuzov, in detailed investigations, established the tautomerism of the dialkyl phosphites and the dual reactivity of their metal derivatives, showing that this dual reactivity cannot be explained by tautomerism in these derivatives. The mechanism of these processes found its explanation in the light of A. N. Nesmeianov's investigations on the conjugation of bonds and the reactivity of organic compounds of various types. The dual reactivity of the metal derivatives of dialkyl phosphites is explained by their ability to react with transfer of the reactive center. M. I. Kabachnik described also the work that he and his coworkers have carried out on the tautomerism of organophosphorus compounds. The solution of many fundamental questions in this field can be found with the aid of his theory of acid-base protolytic tautomeric equilibrium. The successful development of these investigations was helped by the analogy, suggested earlier by A. E. Arbuzov, between dialkyl phosphites and keto-enols. Consideration was given also to the tautomerism of organosulfurphosphorus compounds and to A. E. Arbuzov's work on the tatutomerism of phosphonoacetic ester and other β-phosphono-carbonyl groupings.

A. I. Razumov, assistant professor at the S. M. Kirov Institute of Chemical Technology, Kazan, read a paper about recent work on the mechanism of the Arbuzov rearrangement. Modern physical and chemical methods of investigation confirm the two-stage character of this reaction. The speaker discussed in detail the analysis of so-called "anomalous" cases of rearrangement in which reaction results in the formation of phosphoric derivatives, e.g. in the reaction of phosphorous esters with halo ketones. The speaker considered that phosphoric derivatives, like phosphonic compounds, must be regarded as normal products of the Arbuzov rearrangement. Depending on the degree of polarization and on the character and degree of conjugation, reaction may take either course, e.g.



When σ,π-conjugation is present in the molecule, reaction with the phosphorous ester may proceed either in the 1,2-position or in the 1,4-position. In conclusion, various examples were cited in support of a broader treatment

of the Arbuzov rearrangement, and the factors affecting reaction rate were also considered.

At the evening meeting Professor A. N. Pudovik discussed the mass of new results obtained by him in collaboration with I. V. Konovalova, T. M. Moshkina, and V. I. Nikitina on the addition of dialkyl phosphites and phosphorothioites to unsaturated cyclic ketones, esters of unsaturated cyclic alcohols, and diene systems activated by an electronegative group. The mechanisms of the main reactions and various side reactions were elucidated.

Special attention was accorded to the very substantial paper of I. D. Neklesova, senior scientific worker at the Kazan Affiliated Institute. She expounded present-day views on the mechanism of the physiological action of organophosphorus compounds and indicated the most probable causes of the great universality of their action. A principal task of investigators in this field consists in discovering rational ways of preparing highly effective insecticides of low toxicity to warm-blooded animals and man. An exposition was given of the main theses in the theory of the phosphorylation of cholinesterases by organophosphorus compounds and the mechanism of the action of systemic insecticides. I. D. Neklesova devoted much attention to the relation of chemical structure to toxicity in organophosphorus compounds. It was emphasized that the field of application of organophosphorus compounds is continually extending and that a given compound may be used for several purposes. Only by close collaboration among chemists, biochemists, and biologists working in various fields can full utilization be made of this very extensive and interesting class of organophosphorus compounds.

On September 28 the participants in the Extramural Session of the Division of Chemical Sciences attended a Celebration Dinner in honor of Academician A. E. Arbuzov. The dinner was held in the Musa Dzhalil' Tatar Theater of Opera and Ballet. Among those present were scientists and representatives of Party, Soviet, and Komsomol organizations. The proceedings were opened by the President of the Academy of Sciences of the USSR, Academician A. N. Nesmeianov. On behalf of the Presidium of the Supreme Soviet of the USSR, the first secretary of the Tatar Regional Committee of the Communist Party of the Soviet Union S. D. Ignat'ev presented Academician A. E. Arbuzov with the Order of Lenin and the Hammer and Sickle gold medal. In accepting this high award, A. E. Arbuzov expressed his great indebtedness to the Communist Party and the Soviet government and declared that he would devote all his experience, strength, and knowledge to the welfare of our fatherland and to the consolidation of peace.

An address on the life and activities of Academician A. E. Arbuzov was given by his student and close collaborator Professor G. Kh. Kamai.

More than a hundred congratulatory letters and more than five hundred telegrams were received from various organizations, institutes, universities, and scientists of the Soviet Union, China, France, Great Britain, the German Democratic Republic, the German Federal Republic, Czechoslovakia, Sweden, and other countries.

By his whole life A. E. Arbuzov has shown how it is possible, while living and working on the periphery, to be always in the center of scientific life and in the vanguard of science.

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Division of Chemical Sciences

January 1958

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SOVIET RESEARCH IN CRYSTALLOGRAPHY

Crystallography is a field in which the Russians have been extremely active for many years. This is exemplified by the fact that they publish a journal, Kristallografiia, devoted entirely to articles on this subject. However, many additional articles on crystallographically interesting subjects are scattered throughout the vast Russian chemical literature. As a service to crystallographers, we are publishing as a collection the 112 articles which have been selected by a crystallographer, as the most important in all issues of Russian chemical journals translated by Consultants Bureau, 1949-1955. These journals are: The Journal of General Chemistry; the Bulletin of the Academy of Sciences, Div. Chem. Sci.; the Journal of Analytical Chemistry; the Journal of Applied Chemistry. This Collection, No. 5 in a series being published in various specialized fields, is described directly below:

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